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The Electrostatic Contribution to Hindered Rotation in Certain Ions and Dipolar Ions in Solution. IV

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The present communication is essentially a refinement of the earlier papers of the same title. This refinement is made possible by adopting particular models to represent the shape of molecular cavities, following Kirkwood and Westheimer. An important consequence of this procedure is that the effective dielectric constants used are no longer constant, but vary with intercharge distance. It is pointed out that a more detailed treatment of the molecular shapes involved should lead to further improved calculations.

I. INTRODUCTION

IN the preceding papers of this series,[1–3] certain calculations were made concerning electrostatic influences on intramolecular rotation and dissociation constants. By assuming that the effective dielectric constants entering into expressions for the electrostatic potential energy were constants, independent of configurational angles, it was possible to avoid any assumptions as to the nature of the molecular cavities involved. Thus, from experimental dissociation constants, *average* effective dielectric constants were obtained and employed in estimating electrostatic contributions to restricted internal rotation.

The obvious next step, and the one to be partially carried out here, is to introduce the refinement of a variable D_E, by adopting a reasonable molecular shape which will determine the nature of the dependence of D_E on the molecular configuration.

The type of model to be used is that proposed by Kirkwood and Westheimer,[4,5] in which charges and dipoles are assumed imbedded in a structureless spherical or ellipsoidal molecular cavity of low dielectric constant D_i, the cavity itself being immersed in a solvent of dielectric constant D.

Since Kirkwood and Westheimer did not take into account internal rotation, the present paper is to a certain extent a refinement of their treatment as well as of the earlier papers of this series. It should be remarked, however, that these authors mentioned explicitly[4] the desirability of such a refinement: "A knowledge of the torque hindering internal rotation would permit a more exact application of our formulas involving a calculation of the average value of ΔpK over all internal configurations of the acids and ions." We assume here, as before, that the torques involved arise from two sources: (1) electrostatic interactions between charges and dipoles; and (2) other restrictions to rotation, such as those found in ethane.

[1] T. L. Hill, J. Chem. Phys. **11**, 545 (1943). Hereafter referred to as I.
[2] T. L. Hill, J. Chem. Phys. **11**, 552 (1943). Hereafter referred to as II.
[3] T. L. Hill, J. Chem. Phys. **12**, 56 (1944). Hereafter referred to as III.
[4] J. G. Kirkwood and F. H. Westheimer, J. Chem. Phys. **6**, 506 (1938).
[5] F. H. Westheimer and J. G. Kirkwood, J. Chem. Phys. **6**, 513 (1938).

Generally it is found, and is to be expected, that D_E increases with increasing intercharge distance ρ. Hence the potential barriers using a variable D_E are larger than for a constant average D_E. For, if

$$\rho_2 > \rho_1 > 0$$

and

$$D_E(2) > D_E(\text{Av.}) > D_E(1) > 0,$$

then

$$\frac{1}{D_E(\text{Av.})}\left(\frac{1}{\rho_1}-\frac{1}{\rho_2}\right) < \left(\frac{1}{\rho_1 D_E(1)}-\frac{1}{\rho_2 D_E(2)}\right).$$

Consequently, it can be said that the D_E's given previously retain their significance as *average* D_E's and are quite useful in connection with the correlation of dissociation constants (see III), but serve only to give an approximate lower bound, or first approximation, in the calculation of electrostatic potential barriers.

The adoption of some simple shape for the molecular cavity, such as a sphere or ellipsoid of revolution, will lead to a second approximation. Fisher-Hirschfelder models are helpful in this connection, but one is limited to surfaces for which the mathematics can be carried out. In some cases, it is clear that a better approximation should be obtained by considering the shape of the molecular cavity, in addition to D_E, as being a function of configurational angles. This latter suggestion is not used in the present paper, however, except in a very superficial way for succinic acid.

II. GENERAL REMARKS

We consider in this section several rather self-evident points which were introduced more or less intuitively in I, II, and III.

Suppose we have charges $e_1, \cdots, e_\nu$ imbedded in a cavity, the equation of whose surface is $f(u, v, w) = 0$, where u, v, and w are coordinates. The charge e_k is located at the point (u_k, v_k, w_k), or, more briefly, (k). Then the electrostatic free energy of interaction between e_j and e_k, W_{jk}, may be given by an expression of the form

$$\begin{aligned} W_{jk} &= \frac{e_j e_k}{D_i r_{jk}} + e_j e_k H_{jk} \\ &= \frac{e_j e_k}{r_{jk}}\left(\frac{1}{D_i} + r_{jk} H_{jk}, \right), \end{aligned} \tag{1}$$

where r_{jk} is the distance between e_j and e_k, and H_{jk} is a function of D, D_i, (j), (k), and $f(u, v, w)$. Furthermore, the total electrostatic free energy W is merely the sum of the separate W_{jk}'s:

$$W = \sum_{k=j+1}^{\nu} \sum_{j=1}^{\nu-1} W_{jk}. \tag{2}$$

Hence, the effective dielectric constant $D_E(jk)$ to be used for the interaction between e_j and e_k is

$$\frac{1}{D_E(jk)} = \frac{1}{D_i} + r_{jk} H_{jk}, \tag{3}$$

regardless of whether or not other charges are present. An equivalent statement is that charge effects on ΔpK's are additive. Clearly, D_E is in general different for different interactions and for different molecular configurations for the same interaction. The above remarks are important in studying molecules such as glutamic acid (see III) in which some ions possess more than two charges.

Another consideration which apparently leads to some intuitive difficulty is the fact that we are and have been using the same dielectric constant D_E in expressions for the electrostatic free energy within the molecule and for ΔpK, the latter involving the removal of a charge to infinity. The point is, of course, that the electrostatic free energy arises in exactly the same way; it is equal to the work necessary to bring the various charges from infinity to their respective positions within the molecule. Thus D_E refers essentially to the same process when used in calculating electrostatic potential barriers and ΔpK's.

III. CALCULATIONS

Calculations are discussed below in which a spherical model is employed for oxalic acid, ethylene diamine, glycine, 1,3-propane diamine, β-alanine, malonic acid, succinic acid, pyrophosphoric acid, and dithionic acid. On examining Fisher-Hirschfelder models it will be seen that, since we are taking into account rotation about bonds, a spherical model in these cases is probably the best simple choice. In every case the center of the sphere is taken as the central atom in the chain, or midway between the two central atoms. An ellipsoid of revolution with charges at the foci as a model for succinic and glutaric acids is found to be unsatisfactory, as is

also a sphere for glutaric acid. Glutamic acid is not included since it possesses several interactions of the glutaric acid type. The previous treatment[3] therefore still holds as a first approximation. An ellipsoid with charges not restricted to the foci might improve the results for several of the above substances. But because of the considerable time required, it has not seemed worth while to make such calculations under present conditions. However, the necessary equations are derived in the Appendix, for possible future use, by an obvious generalization of previous work of Westheimer and Kirkwood.[5]

In all the calculations below, the summation method, introduced and discussed in III, will be employed rather than integrations. This will eliminate the necessity of using approximate functions for $D_E(jk)$ as well as for $1/r_{jk}$ (see the discussion in this section concerning glycine). Instead D_E may be calculated directly for each configuration used. Equation (11),[3]

$$K=K^0\frac{\sum_{j=1}^{k}\exp\left(-U_j^i/RT\right)}{\sum_{j=1}^{k}\exp\left(-U_j^a/RT\right)}, \qquad (4)$$

is suitable for all substances treated here except pyrophosphoric and dithionic acids (see below). As before, unless otherwise mentioned, the summation is over staggered arrangements, which are generally believed to be more stable than lined up (eclipsed) arrangements.

Since the energy of interaction between any two charges, and therefore also the effective dielectric constant, is independent of the presence of other charges, it suffices to consider the special case of just two charges e_1 and e_2 present in the molecular cavity. Following Kirkwood and Westheimer,[4] we take $f(u, v, w)=0$ as a sphere of radius b, with internal dielectric constant $D_i=2.00$. Let e_1 and e_2 be joined to the center of the sphere by straight lines of lengths r_1 and r_2, respectively; θ is the angle between the two lines. The sphere is immersed in a solvent of dielectric constant $D(=78$ for water). For the special case $r_1=r_2$, corresponding to Eq. (3), Kirkwood and Westheimer found the sufficiently accurate expression

$$\frac{1}{D_E}=\frac{f_1}{D}+\frac{f_2}{D_i},$$

$$f_1=\frac{2[2x(1-\cos\theta)]^{\frac{1}{2}}}{(1-2x\cos\theta+x^2)^{\frac{1}{2}}}-\frac{[2x(1-\cos\theta)]^{\frac{1}{2}}}{x}\times\ln\frac{(1-2x\cos\theta+x^2)^{\frac{1}{2}}+x-\cos\theta}{1-\cos\theta}, \qquad (5)$$

$$f_2=1-\frac{[2x(1-\cos\theta)]^{\frac{1}{2}}}{(1-2x\cos\theta+x^2)^{\frac{1}{2}}},$$

where $x=r_1^2/b^2$. If $r_1\neq r_2$, we substitute r_1r_2/b^2 for r_1^2/b^2 and replace

$$[2x(1-\cos\theta)]^{\frac{1}{2}} \text{ by } \left\{2x\left[\frac{1}{2}\left(\frac{r_1^2+r_2^2}{r_1r_2}\right)-\cos\theta\right]\right\}^{\frac{1}{2}}.$$

For the molecules considered here r_1 and r_2 are constants over all configurations for a given compound, and $\cos\theta$ may be calculated from structural parameters (given in earlier papers of the series) for each configuration. Thus, from Eq. (5), D_E for a particular configuration may be considered a function of the parameter b (or $\sqrt{x}$), the radius of the molecular cavity. Our procedure will therefore be to adjust b so that Eq. (4) holds (the method is somewhat more complicated for pyrophosphoric and dithionic acids), where b, of course, has a constant value over all configurations. The volume of the cavity V_S may then be calculated from b and compared with the volume V_T found by Traube's rule.[4] It will be noted that whereas Kirkwood and Westheimer referred their distances to dissociable protons, we employ actual intercharge distances.

For an ellipsoid (prolate spheroid) $\lambda=\lambda_0$ with charges at the foci, the procedure is quite similar using the equations of Westheimer and Kirkwood.[5] R, the intercharge distance (and distance between foci), is computed for each configuration. Then, since $\lambda_0^3-\lambda_0=6V/\pi R^3$ and $D_E=D_E(\lambda_0)$, where V is the volume of the cavity, V replaces b as an adjustable parameter (V remaining constant over all configurations).

It was found very convenient to redraw Fig. 1 of reference 4 on a large scale and to include a curve for $\cos\theta=\frac{1}{2}$. Then, for a given value of $\sqrt{x}$, the values of D_E for $\cos\theta$ equal to -1, $-\frac{1}{2}$, 0, and $\frac{1}{2}$ were plotted against $\cos\theta$ and a smooth curve drawn, making possible sufficiently accurate interpolations of D_E for any value of $\cos\theta$ (for the given value of $\sqrt{x}$).

Oxalic Acid

On examining the ΔpK's, from the first and second dissociation constants, in the series of normal dicarboxylic acids, one observes that the values for oxalic and malonic acids are unexpectedly high. This has been discussed in detail elsewhere.[6] It was suggested that in the intermediate ion of both of these acids there exists an appreciable amount of hydrogen bonding, and that there is resonance involving carbon-carbon double bond character in the oxalate ion. These factors tend to make planar configurations most important in the ionic equilibria. Consequently, in the attempt here to improve the previously calculated values of electrostatic hindering potentials, we shall consider only the planar configuration [in Eq. (4)] for both oxalic and malonic acids.

The above discussion must also affect our choice of ΔpK. Obviously ΔpK should be corrected, if possible, to include statistical and electrostatic factors only. By extrapolation of the pK values of Gane and Ingold[3,6,7] for those dicarboxylic acids higher in the series than malonic acid, the predicted values for ΔpK for oxalic and malonic acids are 2.60 and 1.60 (0.60 is the statistical contribution), respectively, instead of the observed values 2.97 and 2.87, respectively. We assume for the present that the discrepancies arise from hydrogen bonding and resonance, and therefore in our calculations the extrapolated values will be used.

We introduce φ here as the rotational angle in place of θ (as in I), since θ has been used in Eq. (5). For the planar configuration $\varphi=0$. The charge distribution and structure of oxalic acid were discussed in I. If r_{12} is the intercharge distance, one finds that

$$r_{12}^2=9.55-2.43\cos\varphi=6.00(1-\cos\theta),$$

whence

$$\cos\theta=0.406\cos\varphi-0.593. \qquad (6)$$

Equations of this type are useful in calculating $\cos\theta$ for the different configurations (values of φ).

The effective dielectric constant D_E may be thought of as a function of $\cos\theta$ and $\sqrt{x}$ instead of $\cos\theta$ and b: $D_E=D_E(\cos\theta,\sqrt{x})$. We shall use the abbreviation $D_E(\cos\theta,\sqrt{x})=\langle\cos\theta\rangle$. Then, applying Eq. (4) to this particular case,

$$10^{-2.00}=0.01$$
$$=\exp\left[-\frac{1}{2}\left(\frac{213.3}{\langle-0.187\rangle}+\frac{164.4}{\langle-1.00\rangle}\right)\right]. \qquad (7)$$

By successive approximations it is found that Eq. (7) is satisfied for $\sqrt{x}=0.813$. The *electrostatic* potential barrier U_0 is then obtained from

$$U_0=|U_{\max}|-|U_{\min}|.$$

For oxalic acid, $U_{\min}$ corresponds to $\varphi=90°$ (staggered), and hence, using $\sqrt{x}=0.813$, D_E must also be evaluated for $\cos\theta=-0.593$. The calculations are summarized in Table I.

It may be mentioned that if the staggered configuration ($\varphi=90°$) is assumed to be the only one appreciably populated, one obtains $\sqrt{x}=0.801$ and the same value for U_0 (220 cal./mole).

Ethylamine Diamine

As has been pointed out before,[2,6] judging from other related ΔpK's, it seems likely that the experimental values available for ΔpK for ethylene diamine and 1,3-propane diamine are appreciably in error. As for oxalic and malonic acids, we shall therefore make our calculations on the basis of ΔpK equal to[8] 2.60 and 1.60, respectively.

Staggered configurations for ethylene diamine are at $\varphi=60°$, 180°, and 300°. Then, from Eq. (4),

$$3\times10^{-2.00}=0.03$$
$$=2\exp\left(\frac{-190.0}{\langle-0.246\rangle}\right)+\exp\left(\frac{-154.0}{\langle-1.00\rangle}\right). \qquad (8)$$

Equation (8) holds for $\sqrt{x}=0.784$. U is a maximum at $\varphi=0°$ and a minimum at $\varphi=180°$. See Table I for details.

Glycine

For this substance, Eq. (4) yields

$$3\times10^{1.99}=293=2\exp\left[\frac{1}{2}\left(\frac{205.0}{\langle-0.161\rangle}+\frac{158.8}{\langle-0.939\rangle}\right)\right]+\exp\left(\frac{177.5}{\langle-0.550\rangle}\right), \qquad (9)$$

whence $\sqrt{x}=0.807$.

[6] T. L. Hill, J. Phys. Chem. (in press).
[7] R. Gane and C. K. Ingold, J. Chem. Soc., p. 2153 (1931).

TABLE I.

	ΔpK (mic.)	$\sqrt{x}$		cos θ	D_E	U_0 (this paper) cal./mole	U_0 (I or II) cal./mole	V_S	V_T A³/molecule	Φ
Oxalic acid	2.00	0.813	$\varphi=0°$:	−0.187	35.9	220	81	40.6	84.4	
			90°:	−0.593	43.9		($\Delta pK_{mic}=2.37$)			
			180°:	−1.000	50.8					
Ethylene diamine	2.00	0.784	$\varphi=0°$:	0.006	25.9	2800	1180	54.6	101	
			60°:	−0.246	30.3		($\Delta pK_{mic}=2.42$)			
			180°:	−1.000	42.2					
Glycine	1.99	0.807	$\varphi=0°$:	−0.101	33.3	−240	−89	45.9	92.5	72.3
			30°:	−0.161	34.1					
			90°:	−0.550	41.1					
			150°:	−0.939	47.9					
			180°:	−1.000	49.8					
1,3-Propane diamine	1.00	0.883	$\varphi', \varphi=0°, 0°$:	0.707	28.2	5400	2310	89.2	127	
			60°, 60°:	0.425	40.5		($\Delta pK_{mic}=1.44$)			
			60°, 300°:	−0.003	54.6					
			60°, 180°:	−0.499	68.3					
			180°, 180°:	−0.994	79.3					
β-Alanine	1.06	0.905	$\varphi', \varphi=0°, 0°$:	0.650	36.9	−1900	−746	79.6	119	97.8
			0°, 180°:	−0.251	72.4					
			180°, 0°:	−0.412	76.5					
			180°, 90°:	−0.697	83.7					
			180°, 180°:	−0.982	89.0					
Malonic acid	1.00	0.933	$\varphi', \varphi=0°, 0°$:	0.581	55.5	310	382	71.2	111	
			90°, 90°:	−0.049	80.1		($\Delta pK_{mic}=2.27$)			
			0°, 180°:	−0.331	88.6					
			90°, 270°:	−0.472	92.4					
			180°, 180°:	−0.962	104.1					
Succinic acid	0.69	0.930	$\varphi=0°$:	0.296	66.0	1060		81.0	138	
			60°:	−0.028	78.4					
			180°:	−1.000	103.7					

From Table I it is evident that D_E may be represented approximately by an equation of the form

$$D_E=a_1(\sqrt{x})-a_2(\sqrt{x})\cos\varphi;\ a_1>a_2>0. \quad (10)$$

Also, the reciprocal of the intercharge distance follows approximately

$$1/r_{12}=b_1+b_2\cos\varphi;\quad b_1, b_2>0. \quad (11)$$

Thus, an equation of the type

$$1/r_{12}D_E\cong c_1(\sqrt{x})+c_2(\sqrt{x})\cos\varphi;\ c_1, c_2>0, \quad (12)$$

could be employed if integrations were used instead of summations. However, it is felt that the errors involved in writing approximate functions for the integration method are more serious than the errors in the summation method, especially for large charge separations. The reason exact functions are not used in the integration method is, of course, that the integrations are too difficult.

1,3-Propane Diamine

The rotational angles here and for β-alanine, malonic acid, and pyrophosphoric acid are φ and φ' instead of θ and θ' as in II. In accordance with the discussion above under ethylene diamine we take ΔpK (microscopic) equal to 1.00. Equation (4) gives

$$9\times10^{-1.00}=0.90$$

$$=2\exp\left(\frac{-217.0}{\langle 0.425\rangle}\right)+4\exp\left(\frac{-134.2}{\langle -0.499\rangle}\right)$$

$$+2\exp\left(\frac{-164.5}{\langle -0.003\rangle}\right)+\exp\left(\frac{-116.7}{\langle -0.994\rangle}\right) \quad (13)$$

from which $\sqrt{x}=0.883$.

β-Alanine

From Eq. (4),

$$9\times 10^{1.06}=103.3$$
$$=2\exp\left[\frac{1}{2}\left(\frac{218.5}{\langle 0.437\rangle}+\frac{134.4}{\langle -0.488\rangle}\right)\right]$$
$$+2\exp\left[\frac{1}{2}\left(\frac{182.0}{\langle 0.188\rangle}+\frac{147.2}{\langle -0.240\rangle}\right)\right]$$
$$+2\exp\left[\frac{1}{2}\left(\frac{145.6}{\langle -0.272\rangle}+\frac{186.0}{\langle 0.222\rangle}\right)\right]$$
$$+2\exp\left[\frac{1}{2}\left(\frac{136.1}{\langle -0.450\rangle}+\frac{117.6}{\langle -0.944\rangle}\right)\right]$$
$$+\exp\left(\frac{126.0}{\langle -0.697\rangle}\right). \quad (14)$$

One finds $\sqrt{x}=0.905$. Only the last value of $\cos\theta$ (-0.697) in Eq. (14) is included in Table I. The others in this equation correspond, respectively, to the following values of φ' and φ: 60°, 30°; 60°, 210°; 60°, 90°; 60°, 270°; 60°, 150°; 60°, 330°; 180°, 30°; and 180°, 210°. The values of D_E in Table I, calculated from $\sqrt{x}=0.905$, are those needed to find U_0. U_0 for the last four compounds in Table I is, of course, the same as W_0 (and not CRT) in II, except for algebraic sign in the case of β-alanine (see the definitions).

Malonic Acid

We take $\Delta pK(\text{microscopic})=1.00$, as mentioned above in the treatment of oxalic acid, and consider only the planar configuration. Then

$$10^{-1.00}=0.100=\exp\left[-\frac{1}{4}\left(\frac{259.5}{\langle 0.581\rangle}+\frac{2\times 149.3}{\langle -0.331\rangle}+\frac{119.9}{\langle -0.962\rangle}\right)\right]. \quad (15)$$

This equation is satisfied for $\sqrt{x}=0.933$.

Succinic and Glutaric Acids

For these acids we make the simplification that the negative charge on a carboxylate group is midway between oxygen atoms.

Treating succinic acid as a sphere, we have

$$3\times 10^{-0.69}=0.612$$
$$=2\exp\left(\frac{-156.3}{\langle -0.028\rangle}\right)+\exp\left(\frac{-112.0}{\langle -1.00\rangle}\right) \quad (16)$$

from which $\sqrt{x}=0.930$. The volume of the sphere, according to this value of $\sqrt{x}$, is 81.0 A^3/molecule, as compared to 138 A^3/molecule from Traube's rule (see Table I).

If the three "minimum" (staggered) configurations of succinic acid are assumed to be ellipsoids of revolution with the same volume but with different values of λ_0 (charges are taken at the foci and therefore the different distances R between foci give different values of λ_0), an equation corresponding to Eq. (16) leads to a volume of about 18 A^3/molecule, which is obviously unsatisfactory. It may be mentioned that the choice of an extended chain as the only important configuration leads to a volume of 65.3 A^3/molecule. Apparently the spherical model is the most satisfactory, but it is certainly too simple.

Neither an ellipsoid with charges at the foci nor a sphere is a possible model for glutaric acid, for in both cases the effective dielectric constants cannot be large enough to fit the experimental value of ΔpK. This can be seen qualitatively by comparing the experimental D_E's given in III with the maximum possible D_E's from the treatments of Kirkwood and Westheimer for a sphere[4] ($D_{E\max}=127.0$) and an ellipsoid having charges at the foci[5] ($D_{E\max}=ca.\ 95$).

Pyrophosphoric Acid

There are nine staggered configurations for pyrophosphoric acid and we may sum over these. On the other hand, we can accomplish the same purpose by taking into account all possible microscopic ions[8] for but a single staggered configuration (assumed rigid). On this latter basis, the number of different microscopic ions will be much greater than if all nine configurations were considered interrelated by possible rotations, but the point is that the increase in number of ions corresponds exactly to the decrease in number of configurations. The two points of view are thus really identical.

The numbering of oxygen atoms (as in II) for the single configuration chosen is of course somewhat arbitrary. We use the following system: position 1 at $\varphi'=300°$; 2 at $\varphi'=60°$; 3 at

[8] T. L. Hill, J. Am. Chem. Soc. **65**, 2119 (1943).

$\varphi'=180°$; 4 at $\varphi=300°$; 5 at $\varphi=60°$; and 6 at $\varphi=180°$.

There are five different types of interactions possible and therefore also five values of $D_E(\cos\theta, \sqrt{x})$. From bond angles and distances given in II, these may be written: $D_{E14}(-0.064, \sqrt{x})$, corresponding to

$$\varphi', \varphi = 60°, 60°;$$
$$D_{E15}(-0.548, \sqrt{x}), \text{ for } \varphi', \varphi = 60°, 300°;$$
$$D_{E16}(-0.849, \sqrt{x}), \text{ for } \varphi', \varphi = 60°, 180°;$$
$$D_{E36}(-0.750, \sqrt{x}), \text{ for } \varphi', \varphi = 180°, 180°;$$

and $D_{E12}(0.515, \sqrt{x})$, for the interaction between two negatively charged oxygen atoms bonded to the same phosphorus atom.

Define

$$\alpha_{jk}=\exp(-\epsilon^2/D_E(jk)r_{jk}kT). \quad (17)$$

Then

$$\begin{aligned}
\alpha_{12}&=\exp(-226.0/\langle 0.515\rangle),\\
\alpha_{14}&=\exp(-152.7/\langle -0.064\rangle),\\
\alpha_{15}&=\exp(-126.6/\langle -0.548\rangle),\\
\alpha_{16}&=\exp(-115.9/\langle -0.849\rangle),\\
\alpha_{36}&=\exp(-119.1/\langle -0.750\rangle).
\end{aligned} \quad (18)$$

The same type of analysis of microscopic ions and equilibrium constants as that in I leads[8] to the following expressions for the six macroscopic dissociation constants:

$$\begin{aligned}
K_{(1)}&=6K_1, \quad K_{(2)}=K_1Y_2/6,\\
K_{(3)}&=2K_1\alpha_{12}Y_3/Y_2,\\
K_{(4)}&=K_1\alpha_{12}Y_4/2Y_3,\\
K_{(5)}&=2K_1\alpha_{12}^2Y_5/Y_4,\\
K_{(6)}&=K_1\alpha_{12}^2Y_6/2Y_5,
\end{aligned} \quad (19)$$

where

$$Y_2=6\alpha_{12}+2\alpha_{14}+2\alpha_{15}+4\alpha_{16}+\alpha_{36},$$
$$Y_3=\alpha_{12}^2+\alpha_{16}^2+2(\alpha_{14}\alpha_{15}+\alpha_{14}\alpha_{16}+\alpha_{15}\alpha_{16}+\alpha_{16}\alpha_{36}),$$

TABLE II. ΔpK's for pyrophosphoric acid.

	$\sqrt{x}$ =0.80	0.825	0.85	0.90	II	K and H[a]	Exp.[b]
$\Delta pK_{(3)-(4)}$	2.06	1.80	1.59	1.40	2.46	2.3	1.1
$\Delta pK_{(4)-(5)}$	5.72	4.63	3.68	2.01	3.15	3.8	4.7
$\Delta pK_{(5)-(6)}$	2.19	1.90	1.67	1.45	2.61	2.7	2.7

[a] See reference 9.
[b] See reference 2.

TABLE III. U_0 (or W_0) for pyrophosphoric acid (cal./mole).

Microscopic ion	Present paper	II
A_{14}	1930	1130
A_{124}	2010	1290
A_{1234}	2120	1270
A_{1245}	2560	1620
A_{12345}	2030	1240
A_{123456}	192	61

$$\begin{aligned}
Y_4&=2\alpha_{12}(2\alpha_{14}\alpha_{15}\alpha_{16}+\alpha_{16}^2\alpha_{36})+4\alpha_{14}\alpha_{15}\alpha_{16}^2\\
&\quad+\alpha_{14}^2\alpha_{15}^2+2\alpha_{14}\alpha_{16}^2\alpha_{36}+2\alpha_{15}\alpha_{16}^2\alpha_{36},\\
Y_5&=\alpha_{14}^2\alpha_{15}^2\alpha_{16}^2+2\alpha_{14}\alpha_{15}^3\alpha_{16}\alpha_{36},\\
Y_6&=\alpha_{14}^2\alpha_{15}^2\alpha_{16}^4\alpha_{36}.
\end{aligned} \quad (20)$$

We may now write theoretical expressions for $K_{(3)}/K_{(4)}$, $K_{(4)}/K_{(5)}$, and $K_{(5)}/K_{(6)}$ which are functions of $\sqrt{x}$. The procedure is therefore to find that value of $\sqrt{x}$ which gives the best agreement between the theoretical and experimental values of these ratios.

Calculations have been made for $\sqrt{x}=0.80$, 0.85, and 0.90. The results are given in Table II together with: (1) the theoretical values from II [$D_E=30$ for all interactions (integration)]; (2) the theoretical values of Kossiakoff and Harker[9] (see II); and (3) the experimental values (see II). After drawing smooth curves for each ΔpK against $\sqrt{x}$, the value $\sqrt{x}=0.825$ is estimated as giving the most satisfactory agreement. The ΔpK values for $\sqrt{x}=0.825$ are included in Table II, as interpolated from the curves. The sum of the absolute deviations of theoretical from experimental values is 1.6 for $\sqrt{x}=0.825$, 2.1 for Kossiakoff and Harker,[9] and 3.0 for $D_E=30^2$. Thus the present refinement seems a good deal more satisfactory than the treatment in II.

In order to compute U_0 for the various ions (considering rotation as being possible but inhibited), we need effective dielectric constants for $\sqrt{x}=0.825$. These are $D_{E14}=36.7$, $D_{E15}=46.9$, $D_{E16}=52.5$, and $D_{E36}=50.8$ for the four configurations (values of φ and φ') previously mentioned. A number of others (*not* corresponding to minima in V) are also necessary and have been calculated but will not be listed here. However, $D_{E12}=21.4$ should be given. Table III compares

[9] A. Kossiakoff and D. Harker, J. Am. Chem. Soc. **60**, 2047 (1938).

previous values of U_0 (called W_0 in II), in which $D_E=30$ for all interactions, with present values.

It is found that c_{14}/c_{12}, the ratio of the concentrations of symmetrical to unsymmetrical pyrophosphoric acid, is 4400 as compared to the earlier value of 28.6. This large increase is a consequence of the considerable variation of D_E with intercharge distance.

Dithionic Acid

The dissociation constants of this strong acid are not known, hence we must assume a value of $\sqrt{x}$.

For a number of relatively simple acids, such as orthophosphoric acid, with a single central atom to which are bonded OH groups, D_E is found to fall between 18 and 23 (see footnote 13, I). These molecules are spherical in shape so that we may apply the equations of Kirkwood and Westheimer.[4] Values of D_E from 18 to 23 correspond to a range in $\sqrt{x}$ of from about 0.70 to 0.75, averaging approximately 0.725. Now dithionic acid (two central atoms) is intermediate in shape between pyrophosphoric acid (three central atoms) and the simple acids (one central atom) mentioned above. In the absence of other information, therefore, we shall adopt here for dithionic acid, $\sqrt{x}=0.775$, which lies halfway between 0.725 and 0.825 (pyrophosphoric acid).

TABLE IV. U_0 for dithionic acid (cal./mole).

Microscopic ion	Present paper	I
A_{14}	2190	960
A_{124}	2040	920
A_{1234}	156	42
A_{1245}	2350	1000
A_{12345}	312	84
A_{123456}	468	126

In considering the various microscopic ions, the same technique is used as for pyrophosphoric acid. The staggered arrangement here is identical with that in ethane. Employing the notation of I, we take positions 1 and 5 *trans* to each other, as are also 3 and 4 and 2 and 6.

There are three D_E's: $D_{E14}(-0.309, \sqrt{x})$, corresponding to $\varphi=60°$; $D_{E15}(-1.00, \sqrt{x})$, for $\varphi=180°$; and $D_{E12}(0.309, \sqrt{x})$, for two oxygen atoms bonded to the same sulphur atom.

Instead of Eq. (18), we have, for $\sqrt{x}=0.775$:

$$\begin{aligned}\alpha_{12}&=\exp(-228.4/19.2)=6.31\times10^{-6},\\ \alpha_{14}&=\exp(-166.1/29.6)=3.65\times10^{-3},\\ \alpha_{15}&=\exp(-134.3/40.2)=3.54\times10^{-2}.\end{aligned}\tag{21}$$

Replacing Eqs. (19) and (20), one finds for dithionic acid

$$\begin{aligned}&K_{(1)}=6K_1,\quad K_{(2)}=K_1Y_2/2,\\ &K_{(3)}=2K_1\alpha_{12}Y_3/3Y_2,\\ &K_{(4)}=3K_1\alpha_{12}\alpha_{14}^2\alpha_{15}Y_2/2Y_3,\\ &K_{(5)}=2K_1\alpha_{12}^2\alpha_{14}^2\alpha_{15}/Y_2,\\ &K_{(6)}=K_1\alpha_{12}^2\alpha_{14}^2\alpha_{15}/6,\end{aligned}\tag{22}$$

in which

$$\begin{aligned}Y_2&=2\alpha_{12}+2\alpha_{14}+\alpha_{15},\\ Y_3&=\alpha_{12}^2+3\alpha_{14}^2+6\alpha_{14}\alpha_{15}.\end{aligned}\tag{23}$$

Equations (21) and (22) give $K_{(5)}/K_{(6)}=2.81\times10^2$ as compared to 1.6×10^3 from Kossiakoff and Harker[9] and 7.56×10^2 from I ($D_E=30$). Also, one finds $c_{1245}/c_{1234}=3380$ as contrasted with 11.9 in I.

It is interesting to note that for pyrophosphoric acid $D_{E12}=21.4$, for dithionic acid $D_{E12}=19.2$, and for a number of simple acids such as orthophosphoric acid (see above), $D_E=18$ to 23. These D_E's are quite similar and all apply to the same type of interaction: two negatively charged oxygen atoms bonded to the same atom.

In Table IV are presented electrostatic potential barriers for dithionic acid, calculated as for pyrophosphoric acid.

DISCUSSION

The more accurate, though still approximate, calculations of U_0 in this paper have resulted in values increased generally by from 50 to 200 percent over earlier ones reported on the basis of constant dielectric constants.

In all compounds studied it is still very likely that the electrostatic contribution to restricted rotation is less important than other contributions, though many values of U_0 are apparently of the order of magnitude of the non-electrostatic part. Care must be taken, in these comparisons, to note the exact meaning of U_0. For example, $U_0=5400$ cal./mole for 1,3-propane diamine (two rotational angles) should be compared with

$2\times3400=6800$ cal./mole rather than with 3400 cal./mole. This latter value is, however, to be compared with $U_0=2800$ cal./mole for ethylene diamine (one rotational angle). $V_0=3400$ cal./mole is, of course, an *estimated* value. The *total* potential energy function restricting rotation is the sum of electrostatic and non-electrostatic parts. In general, the two components may differ in phase, frequency, and amplitude (see Table I of I and Table I of II).

Concerning the validity of the summation procedure, it should be emphasized that the relative magnitude of U_0 and V_0 is not significant; rather, it is the ratio V_0/RT which is important. From our present knowledge it would appear that V_0 is generally from two or three to six times as large as RT (at room temperature). Furthermore, inasmuch as the k configurations with minimum V are symmetrically distributed and often fairly numerous, an average is obtained in any case which is a good approximation to the ideal average over all angles.

For the organic compounds studied, we may compare the volumes calculated from b (V_S) with those obtained by Traube's rule (V_T). For compounds with α charge interactions, V_S is approximately one-half of V_T, with a ratio of radii $b_S/b_T\leqq0.8$. For β and γ interactions, V_S is roughly 0.6 or 0.7 of V_T and $b_S/b_T\leqq0.9$. Thus, the parameter b_S found in the calculations of this paper from dissociation constants and spherical models is in fairly good agreement with b_T from Traube's rule. It may be remarked that for glycine and β-alanine the experimental apparent molal volumes[10] Φ are intermediate between V_S and V_T (see Table I).

In III an approximate empirical relationship, valid for a number of compounds, was found between *average* D_E's and the number of carbon atoms between charges. It is not surprising to find, however, that there is no such general relationship, extending over a number of compounds, between $D_E(\cos\theta, \sqrt{x})$ and intercharge distance.

In conclusion, in addition to possible refinements mentioned above, several obvious extensions may be suggested. Analogous calculations for dipoles, rather than charges, may be carried out. Also, detailed calculations should be made for solvents other than pure water. In both of these cases it would be interesting to see if the parameter b_S retains approximately the same value in the same or similar compounds.

[10] E. J. Cohn and J. T. Edsall, *Proteins, Amino Acids, and Peptides as Ions and Dipolar Ions* (Reinhold Publishing Corporation, New York, 1943).

APPENDIX

The object here is to derive an expression for D_E, for future use, which will apply to arbitrary charge distributions in molecules resembling ellipsoids of revolution (prolate spheroids). We use confocal elliptical (prolate spheroidal) coordinates and follow the general procedure of Westheimer and Kirkwood,[5] who considered charges restricted to the line joining the foci.

Laplace's equation for the potential ψ is

$$(\lambda^2-1)\frac{\partial^2\psi}{\partial\lambda^2}+2\lambda\frac{\partial\psi}{\partial\lambda}+(1-\mu^2)\frac{\partial^2\psi}{\partial\mu^2}-2\mu\frac{\partial\psi}{\partial\mu}+\frac{\lambda^2-\mu^2}{(1-\mu^2)(\lambda^2-1)}\frac{\partial^2\psi}{\partial\varphi^2}=0. \quad (24)$$

Then, if $\psi_i(\lambda, \mu, \varphi)$ and $\psi_e(\lambda, \mu, \varphi)$ are potentials which satisfy this equation at points inside and outside the ellipsoid $\lambda=\lambda_0$, respectively, we may write

$$\psi_i=\frac{1}{D_i}\sum_{k=1}^{\nu}\frac{e_k}{|\mathbf{r}-\mathbf{r}_k|}+\sum_{n=0}^{\infty}\sum_{m=0}^{n}P_n^m(\mu)P_n^m(\lambda)\times(B_{nm}\cos m\varphi+B'_{nm}\sin m\varphi) \quad (25)$$

and

$$\psi_e=\sum_{n=0}^{\infty}\sum_{m=0}^{n}P_n^m(\mu)Q_n^m(\lambda)(A_{nm}\cos m\varphi+A'_{nm}\sin m\varphi), \quad (26)$$

where $|\mathbf{r}-\mathbf{r}_k|$ is the distance between (λ, μ, φ) and the point $(\lambda_k, \mu_k, \varphi_k)$, at which is located the kth of the ν charges e_k. The P_n^m and Q_n^m are associated Legendre functions of the first and second kinds, respectively. We shall use the expansion[11]

$$\frac{1}{|\mathbf{r}-\mathbf{r}_k|}=\frac{2}{R}\sum_{n=0}^{\infty}\sum_{m=0}^{n}D_{nm}P_n^m(\lambda_k)Q_n^m(\lambda)\times P_n^m(\mu_k)P_n^m(\mu)\cos m(\varphi-\varphi_k);\ \lambda_k<\lambda, \quad (27)$$

where

$$D_{nm}=(-1)^m(2-\delta_{0,m})\frac{2n+1}{2}\left[\frac{(n-m)!}{(n+m)!}\right]^2 \quad (28)$$

and R is the interfocal distance

By making use of the usual boundary conditions and orthogonality properties we obtain

$$\frac{2}{D_iR}D_{nm}Q_n^m(\lambda_0)\beta_{nm}+P_n^m(\lambda_0)B_{nm}=Q_n^m(\lambda_0)A_{nm}, \quad (29)$$

$$\frac{2}{D_iR}D_{nm}Q_n^m(\lambda_0)\beta'_{nm}+P_n^m(\lambda_0)B'_{nm}=Q_n^m(\lambda_0)A'_{nm}, \quad (30)$$

$$\frac{2}{R}D_{nm}Q_n^{m\prime}(\lambda_0)\beta_{nm}+D_iP_n^{m\prime}(\lambda_0)B_{nm}=DQ_n^{m\prime}(\lambda_0)A_{nm}, \quad (31)$$

$$\frac{2}{R}D_{nm}Q_n^{m\prime}(\lambda_0)\beta'_{nm}+D_iP_n^{m\prime}(\lambda_0)B'_{nm}=DQ_n^{m\prime}(\lambda_0)A'_{nm}, \quad (32)$$

[11] Y. Sugiura, Zeits. f. Physik **45**, 484 (1927). The author is indebted to Professor F. H. Westheimer for providing this reference.

where

$$\beta_{nm}=\sum_{k=1}^{p} e_k P_n^m(\lambda_k)P_n^m(\mu_k)\cos m\varphi_k, \quad (33)$$

$$\beta'_{nm}=\sum_{k=1}^{p} e_k P_n^m(\lambda_k)P_n^m(\mu_k)\sin m\varphi_k. \quad (34)$$

Then, from Eqs. (29) to (32),

$$B_{nm}=\frac{2D_{nm}\beta_{nm}}{R}\left(\frac{1}{D}-\frac{1}{D_i}\right)\left[\frac{P_n^m(\lambda_0)}{Q_n^m(\lambda_0)}-\left(\frac{D_i}{D}\right)\frac{P_n^{m\prime}(\lambda_0)}{Q_n^{m\prime}(\lambda_0)}\right]^{-1}=f(\beta_{nm}), \quad (35)$$

$$B'_{nm}=f(\beta'_{nm}). \quad (36)$$

The electrostatic free energy of the molecule is

$$W=\frac{1}{2}\sum_{k=1}^{p} e_k\psi_i(\lambda_k,\mu_k,\varphi_k), \quad (37)$$

where $\psi_i(\lambda_k,\mu_k,\varphi_k)$ is the value of ψ_i at $(\lambda_k,\mu_k,\varphi_k)$ due to all charges except e_k. W can be written as the sum of the separate contributions of each possible interaction, as in Eqs. (1) and (2). Then, corresponding to Eq. (3), for the interaction between the jth and kth charges

$$\frac{1}{D_E(jk)}=\frac{1}{D_i}+2\left(\frac{r_{jk}}{R}\right)\left(\frac{1}{D}-\frac{1}{D_i}\right)\times\sum_{n=0}^{\infty}\sum_{m=0}^{n} P_n^m(\mu_j)P_n^m(\lambda_j)P_n^m(\mu_k)P_n^m(\lambda_k)\times T_{nm}(\lambda_0)\cos m(\varphi_j-\varphi_k) \quad (38)$$

in which

$$T_{nm}(\lambda_0)=D_{nm}\left[\frac{P_n^m(\lambda_0)}{Q_n^m(\lambda_0)}-\left(\frac{D_i}{D}\right)\frac{P_n^{m\prime}(\lambda_0)}{Q_n^{m\prime}(\lambda_0)}\right]^{-1} \quad (39)$$

and r_{jk} is the distance between e_j and e_k. Recurrence formulas are found to be of considerable aid in applying Eq. (38).

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Raman Spectra of Acetylenic Bromides, Iodides, and Ketones and of Some Cyclic Compounds

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Raman spectra are listed for series of acetylenic bromides, iodides, and ketones, and for ascaridole, 1,3-dioxane, ethyl-*p*-toluenesulfonate, and for the *cis*- and *trans*-1,2-diacetoxycyclohexanes. Depolarization factors (when obtained) and relative intensities were measured by use of a Gaertner microdensitometer.

DURING the course of several investigations carried on in this laboratory, there have been obtained the Raman spectra of a miscellany of compounds, data for which do not appear in the literature. Part of the work reported here represents preliminary investigations on series of compounds whose spectra did not exhibit the particular anticipated qualities. Other spectra were obtained on intermediates employed in the synthesis of diverse compounds.

The method of obtaining the spectra has been described elsewhere.[1] The results are listed in Tables I–III, in which $\Delta\nu$ is given in cm^{-1}; ρ is the depolarization factor and I is the intensity measured by use of a Gaertner microdensitometer; D and P represent lines that were depolarized or polarized, respectively, but for which no accurate measurement could be made; w is the designation for lines too weak for densitometer readings; and b means an unusually broad line. In each case the strongest line on the plate is arbitrarily given an intensity of 100.

ACETYLENIC BROMIDES[2]

R—C≡C—Br

These halides, whose spectra are listed in Table I, were prepared by the general method of Straus, Kollek, and Heyn.[3] It was found unnecessary, however, to use soap for emulsifying the hydrocarbon provided the reaction mixture was stirred vigorously.

[1] F. F. Cleveland, M. J. Murray, J. R. Coley, and V. I. Komarewsky, J. Chem. Phys. **10**, 18 (1942).

[2] For the spectrum of the first member of this series see F. F. Cleveland and M. J. Murray, J. Chem. Phys. **11**, 450 (1943).

[3] F. Straus, L. Kollek, and W. Heyn, Ber. **B63**, 1868 (1930).

TABLE I. Raman spectra of acetylenic bromides and iodides.

$C_2H_5C\equiv CBr$		$C_2H_5C\equiv CI$			$C_3H_7C\equiv CBr$		$C_3H_7C\equiv CI$		$C_4H_9C\equiv CBr$			$C_4H_9C\equiv CI$		$C_5H_{11}C\equiv CBr$		$C_5H_{11}C\equiv CI$			$C_6H_5C\equiv CBr$	
$\Delta\nu$	I	$\Delta\nu$	I	ρ	$\Delta\nu$	I	$\Delta\nu$	I	$\Delta\nu$	I	ρ	$\Delta\nu$	I	$\Delta\nu$	I	$\Delta\nu$	I	ρ	$\Delta\nu$	I
263	13	242	10	0.7	255	3	227	w	249	3	P	230	3	241	w	218	2		267	w
351	16	349	20	0.8	347	30	341	28	341	18	0.75	346	20	346	35	346	13	0.6	356	w
		380	8	0.4			378	6	370	2	P					380	w			
417	7	417	w		417	6	406	6	417	1		417	1							
									452	1		450	w							
545	1	530	3	0.9			543	2	567	1	P	559	1	564	1	554	2	D		
																			622	w
704	w	701	w																	
780	2	782	2	0.8					807	2	0.31	811	3							
					846	2	846	4	852	w				835	2	832	2	P	837	w
					878	2	877	6	871	1	P	876	1							
908	8	892	2	0.7					895	1	P	896	1							
									926	1		923	1							
							964	w	947	1		955	1			964	w			
							1002	w								987	w		999	10
1046	16	1037	6	0.5	1062	w	1056	2	1064	3	0.4	1060	3	1047	w	1041	1			
1080	5	1074	3	0.6										1073	w	1071	2			
					1091	3	1094	5	1100	5	0.55	1104	5	1112	2	1108	2	0.7	1178	3
							1227	w	1238	1		1239	w						1229	12
1260	w	1256	1	0.9			1262	2				1280	w							
									1291	2	D	1299	1	1302	5	1301	2			
1318	14	1314	6	0.8	1325	w	1327	6	1324	5	0.55	1324	7	1328	5	1326	3	0.7		
1382	3	1380	1	0.8			1355	w												
1436	11	1433	5	0.7	1428	4	1427	8	1430	8	0.9	1427	7	1435	15	1435	6	0.7		
1461	11	1458	3	0.7	1453	4	1451	7	1446	7		1448	6	1458	10	1455	4		1597	32
2114	w	2101	w																	
		2186	100	0.3			2192	100				2190	100			2191	100	0.3		
2210	100	2212	18	0.4	2217	100			2215	100	0.38			2219	100				2201	100
2224																				
2734	w	2732	w	P					2732	w										
2842	9	2840	3	0.2	2828	w	2832	5	2830	3	P	2826	3	2854	20	2861	20b	0.25		
2881	17	2882	12	0.3	2873	25	2869	17	2863	22	0.3	2863	20	2867	40					
2920	60	2912	35	0.3	2909	40	2903	50	2904	50	0.47	2905	50	2905	70	2904	50	0.3		
2938	50	2937	25	0.3	2935	40	2933	40	2928	45	0.33	2929	20	2928	60	2926	30	0.3		
2986	22	2982	15	0.9	2966	10	2966	9	2961	12	0.62	2964	5	2967	15	2961	10	0.6	3062	15

1-Bromo-1-butyne,

C_2H_5—C≡C—Br, b.p. 90–91° at 750 mm.

1-Bromo-1-pentyne,

C_3H_7—C≡C—Br, b.p. 117° at 750 mm.

1-Bromo-1-hexyne,

C_4H_9—C≡C—Br, b.p. 74° at 72 mm.

1-Bromo-1-heptyne,

C_5H_{11}—C≡C—Br, b.p. 71–73° at 22 mm.

1-Bromo-2-phenylethyne,

C_6H_5—C≡C—Br, b.p. 68–69° at 3 mm.

ACETYLENIC IODIDES[2]

R—C≡C—I

These halides, whose spectra are also listed in Table I, were prepared from the acetylenic Grignard reagent by the action of iodine in ether solution. The method is that of Grignard and Perrichon.[4]

1-Iodo-1-butyne,

C_2H_5—C≡C—I, b.p. 65.5–66.0° at 75 mm.

1-Iodo-1-pentyne,

C_3H_7—C≡C—I, b.p. 75–76° at 45 mm.

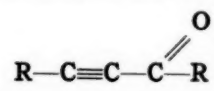
1-Iodo-1-hexyne,

C_4H_9—C≡C—I, b.p. 74° at 16 mm.

1-Iodo-1-heptyne,

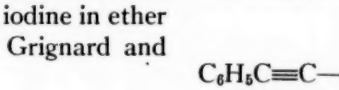
C_5H_{11}—C≡C—I, b.p. 91° at 18 mm.

ACETYLENIC KETONES[5]



These ketones were prepared and their spectra obtained by R. E. Dineen. The synthetic method used was that of Kroeger and Nieuwland,[6] in which an anhydride is reacted with the aryl- or alkylacetylenemagnesium chloride.

1-Phenyl-1-butyn-3-one,



$C_6H_5C\equiv C-C-CH_3$, b.p. 79.0–79.4° at 2 mm, n_D^{24} 1.5730.

[4] V. Grignard and H. Perrichon, Ann. Chim. Phys. **5**, 5 (1926).

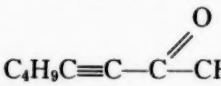
[5] For the spectrum of 6-dodecyn-5-one, see M. J. Murray and F. F. Cleveland, J. Am. Chem. Soc. **63**, 1363 (1941).

[6] J. W. Kroeger and J. A. Nieuwland, J. Am. Chem. Soc. **58**, 1861 (1936).

TABLE II. Raman spectra of acetylenic ketones.

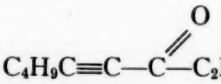
1-Phenylbutyn-3-one Δν	I	ρ	3-Hexyn-2-one Δν	I	3-Octyn-2-one Δν	I	ρ	4-Nonyn-3-one Δν	I	ρ
167	1.0		193	6b	207	1b				
208	0.7		226	8b	261	w				
296	0.2				319	3				
364	2		357	3b	354	7b		349	2b	0.8
395	0.3				378	4		371	2	
435	1.0		406	1b	423	1		428	½b	
469	0.3				441	2				
514	0.7		511	1						
533	1.7									
583	1.5		585	3	587	4				
590	1.2									
622	1.7		659	3	658	1		626	w	
678	1.1									
759	1.4		782	½	809	3b		804	2	0.3
					872	1		870	w	
852	1.4		906	½	898	1		892	w	
					924	1		926	2	P
978	18	0.22	974	20	948	4		958	½	
					974	10b				
997	15	0.15								
1026	0.9		1037	3				1013	1	
								1047	2b	0.6
1063	0.2		1068	3	1059	4		1071	1	
1156	25	0.3			1106	7		1105	2	0.8
								1173	w	
1178	2				1234	3		1235	½	
1264	6b	0.35			1299	1		1295	1	D
			1314	3	1325	6		1323	2	D
			1376	2	1356	1				
1442	0.7		1430	8	1424	8	D	1421	4b	D
1492	6	0.5	1460	6	1446	7	D	1451	5b	D
1593	60	0.4								
1684	33	0.3	1676	75	1675	100	0.4	1674	30	0.4
2125	7	0.4								
2169	w				2170	w				
2205	100	0.4	2211	100	2212	100	0.4	2212	100	0.4
			2227	30						
2257	w		2269	2	2262	4		2247	5	
2342	w									
2448	w									
2498	w									
2561	0.7									
					2824	w				
			2885	10	2863	20	P	2865	30	
2917	5	0.2	2919	75	2910	100b	0.4	2903	60	
			2941	30	2934	40		2937	70	
2965	w				2964	15	D	2977	13	
3000	w		2990	10b	3007	4				
3064	8	0.45								
3184	0.4									

3-Octyn-2-one,



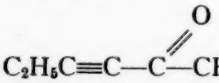
$C_4H_9C{\equiv}C{-}C{-}CH_3$, b.p. 75–77° at 14–16 mm, n_D^{23} 1.4459.

4-Nonyn-3-one,



$C_4H_9C{\equiv}C{-}C{-}C_2H_5$, b.p. 92–94° at 15 mm, n_D^{23} 1.4484.

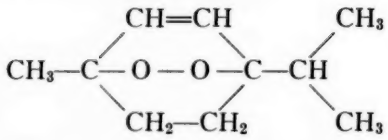
3-Hexyn-2-one,



$C_2H_5C{\equiv}C{-}C{-}CH_3$, b.p.[7] 77.0–78.5° at 73 mm, n_D^{25} 1.4371.

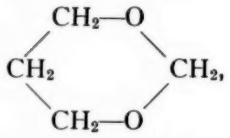
[7] The boiling point of 76° at 15 mm and n_D^{25} 1.4460 as given for this compound by J. W. Kroeger, F. S. Sowa, and J. A. Nieuwland, J. Org. Chem. **1**, 163 (1936) appear to be in error since these are almost exactly the same boiling point and index of refraction given by Kroeger and Nieuwland (reference 6) and by the present investigators for 3-octyn-2-one.

ASCARIDOLE



The sample investigated was an Eastman Kodak Company product. It was distilled in vacuum directly into the Raman tube with no attempt at fractionation.

1,3-DIOXANE



1,3-Dioxane (trimethyleneformal).

The sample used was an Eastman Kodak Company product which was carefully fractionated, b.p. 104.7–105.0° at atmospheric pressure. The spectrum, listed in Table III, was obtained by R. H. Saunders.

TABLE III. Raman spectra of some cyclic compounds.

1,2-Diacetoxycyclohexane *cis* Δν	I	*trans* Δν	I	1,3-Dioxane Δν	I	ρ	Ascaridole Δν	I	Ethyl *p*-toluenesulfonate Δν	I	ρ
234	2b	217	1						229	20	0.3
285	w	248	w								
318	3	276	1	273	2	D	315	w	336	w	
361	1	365	4						373	7	0.7
381	1										
430	1	441	1	439	2	P	438	2			
467	1			461	4	D	463	4	477	w	0.8
503	1	531	4	491	7	0.6	547	1			
568	3	559	1				583	1			
605	2	604	1						633	20	0.9
626	2	638	2	649	w	D			657	3	
666	1	661					728	30	751	w	
792	2	798	2						791	30	0.15
821	4	815	w				816	4	810	14	0.3
849	1	842	2	834	100	0.2	878	6			
884	3	892	4	905	8	0.7	893	4			
921	2b	914	3				938	w			
954	1	957	1	988	35	0.25					
986	2	991	1								
1015	w			1011	10	D					
1029	5	1040	4	1046	6	D					
1055	w	1060	3				1064	1			
1072	2	1100	w	1092	10	D			1099	25	0.25
1122	1						1128	7			
1147	1	1148	4	1154	7	D			1173	100	0.2
1172	w								1188	25	
1207	1	1216	2	1207	4	D	1207	5	1210	3	
1257	4	1249	3	1230	7	D					
		1271	w	1296	20	D					
		1300	w	1312	15				1349	w	
1310	2	1318	w				1312	w	1380	7	P
1343	2b	1354	2	1408	w	D	1344	w			
1386	2	1388	2	1423	10	D	1380	w	1445	4	
1448	4	1449	6	1463	30	D	1450	12	1462	4	
1735	3	1734	4	2747	4		1623	12	1598	60	0.75
2856	12	2865	18	2783	10	0.15	2874	40	2764	w	P
2910	10	2905	10	2852	80b	0.25	2934	100	2928	30	0.15
				2926	50	0.35			2982	6	0.7
2943	100b	2945	100b	2958	30		2961	65	3038	3	
				2985	75b	0.4	3051	17	3070	18	0.5

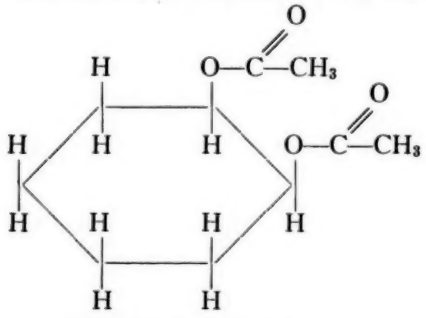
ETHYL *p*-TOLUENESULFONATE

Ethyl *p*-toluenesulfonate,

$$CH_3—C_6H_4—SO_2OC_2H_5.$$

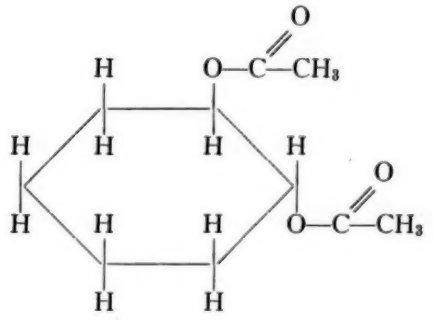
Prepared by Charles Jones by the action of an ether solution of *p*-toluenesulfonylchloride on ethyl alcohol in the presence of sodium hydroxide. B.p. 143° at 2–3 mm. The spectrum is given in Table III.

cis- AND *trans*-1,2-DIACETOXYCYCLOHEXANE



cis-1,2-Diacetoxycyclohexane.

Synthesized by acetylation of the corresponding *cis*-glycol by Howard Hess, who also obtained the spectrum of the compound. B.p. 117.8–118.0° at 12 mm, n_D^{25} 1.4475.



trans-1,2-Diacetoxycyclohexane.

Synthesized by the action of silver acetate on the *trans*-bromohydrin by Robert Buckles, who also obtained the spectrum of this compound. B.p. 119.8–120.0° at 12 mm, n_D^{25} 1.4458.

ACKNOWLEDGMENT

The authors wish to acknowledge the work of the several students who prepared and obtained the spectra of a number of the compounds.

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Accommodation Coefficients on Gas Covered Platinum *

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(Received March 1, 1944)

Accommodation coefficients on a platinum wire have been computed for five monatomic and five diatomic gases from Pirani gauge measurements at room temperature, 18.9° to 30.5°C. Through careful control of experimental conditions it was possible to apply exact theoretical relations for the effects of radiation, wire conduction, and free molecule conduction upon the temperature distribution along the gauge wire. For each of the gases the accommodation coefficient increases with pressure up to about 0.1 mm and then remains constant throughout the pressure range in which complete free molecule conduction exists, indicating the absence of complete gas saturation of the wire surface at the lower pressures. There is no detectable temperature coefficient in the small interval in which measurements were made. At room temperature the mean accommodation coefficients on a completely gas covered platinum wire are: helium, 0.403±0.001; neon, 0.700±0.002; argon, 0.847±0.002; krypton, 0.844±0.002; xenon, 0.858±0.002; hydrogen, 0.312±0.001; deuterium, 0.393±0.001; nitrogen, 0.769±0.002; carbon monoxide, 0.772±0.002; oxygen, 0.782±0.002.

ACCURATE values of accommodation coefficients of gases on solids are required for the estimation of energy transport by gases at low pressures. Values for gas covered platinum wire are of particular interest since a heated platinum wire is used frequently as an energy

* Contribution from the Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology, No. 506.

source in pressure measuring devices such as Pirani gauges. Since the physical constants of platinum are very well known, the response of such a gauge as a function of pressure for a given gas can be predicted with accuracy if reliable values are available for the accommodation coefficient.

Thomas and Olmer[1] have recently published values of accommodation coefficients on gas covered platinum. Although they appear to have analyzed correctly the heat flow problem, their values are not considered characteristic of completely gas covered platinum by the present authors because of the low pressures (less than 0.05 mm) used in their experiments. The present results show that for many of the gases they studied saturation of the platinum surface is not attained at pressures less than about 0.1 mm and that at lower pressures the accommodation coefficients increase with pressure. The excellent summaries and discussions of the available

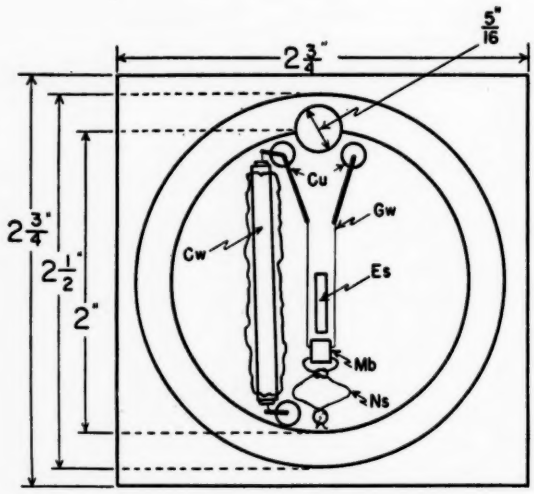

FIG. 1. Details of conductivity gauge.

information on accommodation coefficients on gas covered platinum given by Thomas and Olmer and by Kennard[2] indicate that reliable experimental values are, in most cases, still to be obtained. The authors feel that it is desirable to present their values, obtained before publication of the paper by Thomas and Olmer, since they believe that the careful control of experimental conditions to permit the analysis of results according to rigorous kinetic theory and heat flow theory and the numerous measurements over a sufficiently wide pressure range to insure surface saturation have resulted in accommodation coefficients of high accuracy.

[1] L. B. Thomas and F. Olmer, J. Am. Chem. Soc. **65**, 1036 (1943).
[2] E. H. Kennard, *Kinetic Theory of Gases* (McGraw-Hill Book Company, Inc., New York, 1938), pp. 320–323.

EXPERIMENTAL

Measurements were made at room temperature on five monatomic and five diatomic gases; helium, neon, argon, krypton, xenon, hydrogen, deuterium, nitrogen, carbon monoxide, and oxygen. Accommodation coefficients were computed from the quantity of heat required to raise by about 2° the average temperature of a bright platinum wire surrounded by gas confined between two parallel brass plates. The conductivity gauge was originally designed to contain gases, at pressures measured by the self-contained compensated Pirani gauge, for the scattering of molecular beams. It was, in effect, a short circular brass cylinder, 2 inches in diameter and about $\frac{1}{8}$ inch high, made of two close fitting parts which were soldered together to make a chamber whose only openings were a $\frac{5}{16}$-inch port for evacuation or admission of gas, a 0.020-inch beam entrance hole, and a narrow exit slot. Figure 1 is a diagram of the gauge with the top cover removed. The gauge wire G_w about 4.5 cm long, is bent into a U around the exit slot E_s and lies in a plane midway between the parallel confining surfaces of the upper and lower sections. Jaws on the bottom face of the lower section close over the exit slot to define a slit 0.0003 inch wide. The ends of the gauge wire are soldered to copper rods *Cu*, which are soldered through Kovar metal sleeves sealed into insulating beads of Corning AJ705 glass. The beads are sealed into other concentric Kovar sleeves which are soldered through the brass case of the unit. At the bend of the U the wire passes through a hole in a supporting block of Mycalex *Mb*, which is anchored to a nickel wire 0.008 inch in diameter bent in the form of a bow spring *Ns*. The spring which exerts light tension on the gauge wire is fastened to the brass case with a small watch screw.

A wire having as closely as possible the resistance of the gauge wire was cut from the same

stock as the gauge wire. It was placed between two strips of mica about 0.0003 inch thick by $\frac{1}{16}$ inch wide and drawn through a thin walled platinum tube that had been previously rolled to an oval cross section. The assembly C_w was then flattened and well soldered to the case. This second wire forms an arm of the Wheatstone bridge and serves to compensate for changes in temperature of the brass case. The other two arms of the bridge are wire wound manganin resistors imbedded in ceresin and enclosed in a vacuum tight brass case which is fastened to the main unit. At 26°C the arms of the bridge have the following resistances; gauge wire R_g, 36.22_0 ohms; compensator R_c, 37.62_4 ohms; manganin resistor R_1, 24.60_1 ohms; manganin resistor R_2, 25.37_3 ohms. At a given case temperature a comparatively small current, depending upon the gas pressure, will raise the temperature of the gauge wire and have no effect upon the temperature of the other arms. When this temperature rise is about 2° the bridge will be in balance, that is, $R_g/R_c = R_1/R_2$.

The complete gauge assembly was placed in a bell jar containing the desired gas at an accurately known low pressure obtained by expansion from a smaller volume at a higher accurately measurable pressure. Figure 2 is a schematic diagram of the system used in the above manner. After evacuating the entire system, a given pressure is obtained in the bell jar by letting gas into F to the desired initial high pressure read on the manometer with a cathetometer. In the experiments using helium, argon, nitrogen, and hydrogen which were compressed in metal cylinders, the gas passed through an oil bubbler and a liquid nitrogen trap before expansion into F. After the initial pressure in F has been read, the manometer is shut off and the desired final pressure in N (and accompanying volumes) is obtained by a series of expansions into E and N from F. All pertinent volumes were carefully determined by appropriate calibrations. Since all parts of the system were not at the same temperature, thermometers were lashed to E and F and suspended inside N.

For a given pressure in N, the current required to balance the bridge is read on a sensitive multirange milliameter ($\frac{1}{4}$ percent full scale accuracy) in series with the bridge. This reading depends primarily upon the pressure in N and to a slight extent upon the temperature of the bridge network. Since the temperature-resistance characteristics of the network are known, it is possible to correct for this temperature effect so that the meter readings become single-valued functions of the pressure for a given gas.

Care was taken to insure that the gases used in the experiments were of very high purity. Helium, originally 96 percent, was passed at 2000 pounds per square inch pressure over

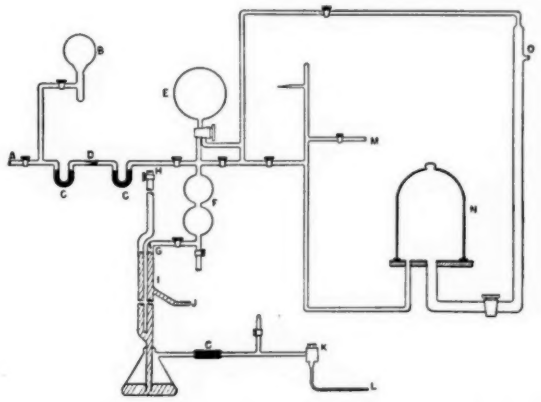

FIG. 2. System for producing and measuring gas pressures. *A*, Connection to gas feed-in system (for helium, argon, hydrogen, nitrogen, and oxygen). *B*, Gas supply (for neon, krypton, xenon, deuterium, and carbon monoxide). *C*, Glass wool filter. *D*, Capillary throttle. *E*, Standard volume (2199 ml). *F*, Standard volume (429.9 ml). *G*, Manometer dead space (2.15 ml). *H*, Connection to vacuum system. *I*, Manometer. *J*, Connection to mercury injector. *K*, Metal stopcock. *L*, Connection to nitrogen tank. *M*, Connection to trap and McLeod gauge (for rough check of pressure). *N*, Bell jar (14,800 ml including connecting tubing). *O*, Connection to trap and vacuum system.

activated charcoal at liquid nitrogen temperature. It is estimated that this produced a final product of at least 99.9 percent purity. The argon, originally 99.9 percent, was passed at 1700 pounds per square inch over activated charcoal at liquid nitrogen temperature. Neon, krypton, and xenon were obtained 99.9 percent pure in Pyrex bulbs from Linde Air Products Company and used without further purification.

Nitrogen, oxygen, and hydrogen were obtained in cylinders from the Puritan Compressed Gas Company, Inc. The nitrogen was 99.5 percent and was passed at atmospheric pressure over activated charcoal cooled with acetone-dry ice mixture. The oxygen and hydrogen were 99.9 percent and were used without further purification. Deuterium was prepared by treating

deuterium oxide, 99.9 percent, with sodium. Carbon monoxide was made by the sulfuric acid-formic acid method and passed through a liquid nitrogen cooled trap into a one-liter storage bulb. It is felt that this procedure should produce gas of at least 99.9 percent purity.

FUNDAMENTAL RELATIONS

The equation for the distribution of temperature along a current bearing wire whose ends are maintained at a fixed temperature has been developed by Roberts[3] and extended by Raines[4] to include a correction for the increase in resistance due to heating of the wire. When the temperature difference Δt between any point on the wire and the surroundings is small so that $4T_0^3\Delta t$ is a sufficiently accurate approximation to $T^4-T_0^4$ (where T is the absolute temperature of a point on the wire and T_0 that of the surroundings or wire ends), the differential equation which equates the rate at which energy is removed from unit length of the wire by radiation, metallic and gaseous conduction to the rate of energy input by electric current is

$$\frac{d^2(\Delta t)}{dx^2}-A(\Delta t)+B=0,$$

for which the solution is:

$$\Delta t=\frac{B}{A}\left[1+\frac{\sinh A^{\frac{1}{2}}(x-l)-\sinh A^{\frac{1}{2}}x}{\sinh A^{\frac{1}{2}}l}\right]. \quad (1)$$

A and B have the values:

$$A=\frac{8\epsilon\sigma(T_0)^3}{rK_{t_0}}+\frac{2}{rK_{t_0}}\left[\frac{1}{2\pi MRT'}\right]^{\frac{1}{2}}\times(C_v+\tfrac{1}{2}R)aP'-\alpha B, \quad (2)$$

$$B=\frac{I^2R_{t_0}}{\pi r^2lK_{t_0}}, \quad (3)$$

where I = heating current in wire, r = wire radius, K_{t_0} = thermal conductivity of the wire at the temperature of the ends, ϵ = total emissivity of bright platinum at room temperature, σ = Stefan-Boltzmann constant, M = molecular weight of gas, R = gas constant per mole, Δt = temperature excess above temperature of the ends, R_{t_0} = resistance of 1 cm of wire at temperature of the ends, α = temperature coefficient of resistance of the wire, C_v = molar heat capacity at constant volume, P' = average gas pressure, T' = average absolute temperature of gas, a = accommodation coefficient, t_0 = centrigrade temperature of the ends or surroundings, T_0 = absolute temperature of the ends or surroundings, and l = length of wire of resistance R_{t_0} at temperature of the ends.

The first term in Eq. (2) arises from heat lost through radiation and the last term from heat gained due to the increase in resistance of the wire with increasing temperature. The second term takes account of the heat lost by free molecule gas conduction. Kennard[5] considers this term in detail and shows that the average absolute temperature of the gas T' is a function of the average absolute temperature of the wire $\bar{T}$, of the absolute temperature of the surroundings T_0 and the accommodation coefficients on the wire and case. Since the accommodation coefficient of the gas on the case is always unity because of the infinite radius of curvature of the case relative to the wire, it is only necessary to take into account the accommodation coefficient of the gas on the wire. Because $\bar{T}$ exceeds T_0 by only 2 degrees, T' may in all cases be taken as the arithmetic mean of $\bar{T}$ and T_0 with a maximum possible error (for the case of the accommodation coefficient of the gas on the wire equal to zero) of 0.3 percent. The average gas pressure in the gauge P' is given by $P_0(T'/T_0)^{\frac{1}{2}}$ where P_0 is the actual pressure in the surroundings at T_0.

From the known characteristics of the Wheatstone network the resistance of the gauge wire at the balance point may be computed. This resistance is a function only of the mean temperature of the wire so that it is the mean temperature excess $\overline{\Delta t}$ which is of interest rather than the temperature excess Δt of a given point on the wire. Substitution of Eq. (1) into the relation

$$\overline{\Delta t}=\frac{1}{l}\int_0^l \Delta t dx$$

gives the following relation for the mean temperature excess of the gauge wire

$$\overline{\Delta t}=\frac{B}{A}\left[1+\frac{2(1-\cosh A^{\frac{1}{2}}l)}{A^{\frac{1}{2}}l\sinh A^{\frac{1}{2}}l}\right]=\frac{B}{A}\left[1-\frac{2\tanh \frac{1}{2}A^{\frac{1}{2}}l}{A^{\frac{1}{2}}l}\right]. \quad (4)$$

[3] J. K. Roberts, Proc. Roy. Soc. **A135**, 192 (1932).
[4] B. Raines, Phys. Rev. **56**, 691 (1939).
[5] E. H. Kennard, reference 2, pp. 311–318.

The accommodation coefficient a is determined from experimental quantities in the following manner. The mean temperature excess at 26°, $\overline{\Delta t}_{26}$, is known from the characteristics of the Wheatstone network. In terms of this standard value the mean temperature excess at any other temperature, Δt_{t_0}, is given by

$$\overline{\Delta t}_{t_0}=\overline{\Delta t}_{26}[1+\alpha(t_0-26)]. \quad (5)$$

This very small variation of the mean temperature excess with temperature is due to the inclusion of the compensator in the bridge. The current through the gauge wire I may be computed from the measured total bridge current and the resistance values of the bridge arms at balance. Thus at a given case temperature and gas pressure $\overline{\Delta t}_{t_0}$ and B are known so that A may be obtained by graphical solution of Eq. (4). Substitution of this A value into Eq. (2) gives a value for a since all other quantities are known.

PHYSICAL CONSTANTS OF THE GAUGE WIRE

The physical constants of the gauge wire must be accurately known if reliable values for the accommodation coefficients are to be obtained. In the present investigation these constants were obtained in the following manner.

A. Length, l

From the same piece of platinum wire of which about 4.5 cm were used in the gauge, about 5 cm were placed between rigid supports and the exact length measured with a cathetometer. The resistance per unit length was determined and from the resistance of the gauge wire the length of the gauge wire was found to be 4.57 cm. This is not the effective length of the gauge, however, since 3 mm of the wire pass through the Mycalex support block. From calculation of the wire conduction loss at zero pressure and estimation of the heat loss through the Mycalex block and supporting wires, it was found that the block was heat stationed at the temperature of the brass case. Thus 3 mm of the wire are not heated by the bridge current and the gauge must be regarded as two separate wires each 2.13_5 cm long whose ends are at the temperature of the case. In Eqs. (1) and (4) the length of the wire l refers to this value. In Eq. (3) it is only necessary that mutually consistent values of R_{t_0} and l be used.

The heat stationing effect of the Mycalex block must also be taken into consideration in evaluating the mean temperature excess of the gauge wire at the bridge balance point. At the reference temperature 26°C, the relation is:

$$\overline{\Delta t}_{26}=\frac{R_1R_c-R_2R_g}{R_2R_g x\alpha}, \quad (6)$$

where x is the fraction of the length of the gauge wire outside the Mycalex block. Insertion of the proper numerical values in Eq. (6) yields 2.114° for $\overline{\Delta t}_{26}$.

B. Temperature Coefficient of Resistance, α

The temperature coefficient of resistance of the gauge wire was found by measuring the resistance at 54.25°C and at 0°C. The average coefficient in this range was found to be 3.63×10^{-3} deg.$^{-1}$.

C. Resistivity, ρ

Matthiessen's rule[6] states that in working a pure platinum wire the resistivity ρ and the coefficient of resistance α may change in value at a given temperature, but only in such manner that the product of the two is constant. By using the values of ρ at 0°C and of α in the range 0°–54.25°C as given for pure platinum in the *International Critical Tables*,[7] ρ at 0°C for the platinum in the gauge wire was found to be 10.694×10^{-6} ohm-cm. Combining this value with the measured α, 3.63×10^{-3}, ρ_{26} for the gauge wire is found to be 11.703×10^{-6} ohm-cm.

D. Radius, r

The radius of the gauge wire as determined from the relation

$$r=\left[\frac{\rho_{26}l}{\pi R_{26}}\right]^{\frac{1}{2}}$$

is 6.86×10^{-4} cm.

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[6] A. Matthiessen and C. Vogt, Pogg. Ann. **122**, 19 (1864).
[7] *International Critical Tables* (McGraw-Hill Book Company, Inc., 1929), Vol. 6, p. 136 (second set of values).

TABLE I.

Gas	t_0 (°C)	I_B (ma)	P (mm)	a
He	25.2	2.205	0.009639	(0.258)
	19.2	2.199	0.01011	(0.296)
	18.9	2.787	0.04097	(0.386)
	22.0	2.959	0.05250	(0.376)
	21.4	3.110	0.06076	(0.392)
	21.8	3.335	0.07714	(0.391)
	29.3	3.645	0.09940	(0.385)
	19.1	3.780	0.1127	0.398
	21.6	4.165	0.1450	0.400
	22.0	4.460	0.1740	0.398
	21.7	4.735	0.1995	0.406
	29.0	4.930	0.2210	0.394
	19.0	5.155	0.2461	0.411
	21.2	5.275	0.2596	0.408
	22.9	5.470	0.2854	0.403
	21.7	5.750	0.3223	0.404
	25.2	5.905	0.3417	0.400
	19.1	6.010	0.3583	0.406
				Mean 0.403
				±0.001
Ne	25.3	2.195	0.01104	(0.466)
	25.5	2.233	0.01374	(0.487)
	27.8	2.740	0.04714	(0.642)
	26.9	2.905	0.06002	(0.659)
	27.4	3.400	0.1018	0.685
	24.2	4.055	0.1709	0.700
	25.1	4.570	0.2322	0.705
	24.9	4.990	0.2900	0.706
	27.8	5.500	0.3669	0.700
	25.6	5.655	0.3940	0.703
	27.2	6.050	0.4671	(0.691)
				Mean 0.700
				±0.002
A	25.6	2.145	0.01095	(0.445)
	26.5	2.215	0.01312	(0.612)
	25.2	2.709	0.05125	(0.807)
	25.9	3.270	0.1045	0.833
	25.3	3.760	0.1589	0.851
	25.6	3.800	0.1643	0.847
	25.6	4.190	0.2157	0.848
	26.7	4.280	0.2252	0.856
	25.3	4.770	0.3015	0.853
	25.9	5.050	0.3497	0.845
	25.6	5.260	0.3883	0.842
				Mean 0.847
				±0.002
Kr	25.8	2.100	0.009823	(0.232)
	28.3	2.510	0.04863	(0.776)
	28.2	2.625	0.06158	(0.800)
	28.2	2.960	0.1040	0.826
	25.7	2.980	0.1077	0.842
	26.0	3.250	0.1451	0.850
	25.8	3.490	0.1818	0.857
	25.6	3.695	0.2173	0.855
	26.0	3.835	0.2451	0.843
	26.0	4.075	0.2914	0.841
	26.1	4.355	0.3484	0.841
	28.2	4.500	0.3764	0.840
	26.1	4.665	0.4165	0.840
	28.2	4.900	0.4766	(0.826)
				Mean 0.844
				±0.002
Xe	26.0	2.080	0.007116	(0.108)
	26.7	2.127	0.01127	(0.454)
	27.4	2.360	0.03784	(0.794)
	25.9	2.527	0.06307	(0.810)
	26.0	2.630	0.07540	(0.848)
	26.0	2.950	0.1250	0.865
	27.4	3.230	0.1725	0.869
	26.0	3.420	0.2111	0.866
	26.1	3.600	0.2524	0.849
	25.9	3.775	0.2891	0.856
	27.2	3.950	0.3352	0.835
	25.7	4.250	0.3986	0.864
				Mean 0.858
				±0.002
H_2	26.5	2.310	0.008717	(0.239)
	25.8	2.350	0.009725	(0.257)
	23.2	3.400	0.04916	(0.309)
	25.9	4.400	0.1013	0.311
	24.0	4.440	0.1027	0.316
	24.0	5.205	0.1536	0.316
	26.7	5.850	0.2039	0.312
	26.6	6.335	0.2479	0.309
	26.3	6.995	0.3111	0.309
	26.0	7.285	0.3434	0.308
				Mean 0.312
				±0.001
D_2	24.8	2.365	0.01162	(0.324)
	25.4	3.300	0.04888	(0.388)
	25.3	3.550	0.06222	(0.386)
	23.6	4.275	0.01041	0.395
	25.3	4.295	0.1056	0.392
	24.9	4.850	0.1439	0.394
	23.5	5.280	0.1767	0.398
	22.1	5.610	0.2048	0.399
	23.3	5.675	0.2112	0.396
	24.7	6.472	0.2903	0.389
	24.8	6.994	0.3470	0.389
	25.5	7.275	0.3804	0.387
	24.5	7.540	0.4148	(0.385)
				Mean 0.393
				±0.001
N_2	25.7	2.225	0.009121	(0.543)
	27.1	2.298	0.01146	(0.625)
	25.5	3.040	0.04950	(0.758)
	26.0	3.670	0.09147	0.765
	25.7	3.784	0.1008	0.761
	26.0	3.910	0.1106	0.761
	25.5	4.440	0.1524	0.784
	26.4	5.030	0.2107	0.776
	25.7	5.100	0.2181	0.775
	24.8	5.765	0.2973	0.767
	25.5	5.985	0.3255	0.763
				Mean 0.769
				±0.002
CO	28.4	2.240	0.008454	(0.586)
	30.0	3.150	0.05471	(0.756)
	28.6	3.700	0.09192	(0.768)
	29.2	4.100	0.1216	0.778
	28.5	4.725	0.1778	0.776
	29.2	5.030	0.2064	0.781
	30.0	5.410	0.2509	0.765
	28.7	5.840	0.3017	0.768
	28.4	6.070	0.3311	0.767
				Mean 0.772
				±0.002

TABLE I.—*Continued.*

Gas	t_0 (°C)	I_B (ma)	P (mm)	a
O_2	30.1	2.220	0.008557	(0.491)
	30.5	3.025	0.05029	(0.742)
	28.7	3.640	0.09046	0.787
	28.8	4.035	0.1226	0.782
	29.6	4.375	0.1520	0.784
	28.3	4.950	0.2080	0.792
	30.5	5.145	0.2306	0.779
	29.2	5.385	0.2579	0.782
	30.1	5.750	0.3054	0.770
	28.6	5.920	0.3259	0.777
				Mean 0.782 ±0.002

E. Thermal Conductivity, K

According to the Wiedemann-Franz relation the ratio of the thermal and electrical conductivities at a given temperature is the same for all pure metals. Therefore, from the values of the resistivity and thermal conductivity[8] of pure platinum and from ρ_0 for the gauge wire, the thermal conductivity K_0 at 0°C for the platinum in the gauge wire may be calculated directly. It has a value of 0.639 watt/cm-degree and varies with temperature according to the relation[8]

$$K_t = K_0[1+0.53\times10^{-3}t].$$

F. Total Emissivity, ε

The total emissivity of bright platinum increases slowly with temperature and at room temperature may be represented with sufficient accuracy from experimental values[9] by the relation

$$\epsilon_T = 0.0359[1+2.6\times10^{-3}(T-300)].$$

RESULTS

All experimental results and derived accommodation coefficients are given in Table I. I_B is the measured total bridge current from which the current through the gauge wire may be calculated. In calculating values for the accommodation coefficients from Eq. (3) the molar heat capacity at constant volume C_v was taken as $\frac{3}{2}R$ or 2.980 calories/mole-degree for each of the rare gases. For the diatomic gases C_v, computed from the molar heat capacities at constant pressure calculated from spectroscopic data,[10] had the following values: hydrogen, 4.909; deuterium, 4.990; nitrogen, 4.973; carbon monoxide, 4.977; oxygen, 5.031 calories/mole-degree. All values are for 300°K with the exception of oxygen which is for 298.1°K. Since the experimental temperatures never differ by more than 8° from these values it was unnecessary to correct the heat capacities for temperature.

At the lower pressures incomplete surface saturation of the wire is quite probably responsible for the low accommodation coefficient values. It seems well established[11] that the accommodation coefficient on a gas free wire is very much lower than that on a gas covered wire. In the present case the low values increase with pressure until they become constant at pressures sufficiently high to insure the presence of a monomolecular gas film on the platinum wire. The lowest pressure at which such surface saturation is attained will not be the same for each of the gases. It appears from Table I, however, that in all cases the accommodation coefficient no longer tends to increase at pressures above about 0.1 mm. Therefore, values below this pressure are placed in parentheses and have been omitted in computing the mean accommodation coefficients (and corresponding probable errors) characteristic of a gas saturated platinum wire. In the case of several gases where measurements were extended to relatively high pressures, there are indications of a decrease in the accommodation coefficient which may be due to the fact that energy transport by the gas is no longer entirely due to free molecule conduction as the mean free path becomes shorter. These values are also enclosed in parentheses and have been excluded in computing means. It should be pointed out that the inclusion of these few high pressure values or the assignment of slightly different values to the pressures at which surface saturation is definitely established would produce changes of at most a few tenths of a

[8] Reference 7, Vol. 5, p. 221 (first set of values).
[9] Reference 8, p. 243.

[10] (a) Hydrogen, C. O. Davis and H. L. Johnson, J. Am. Chem. Soc. **56**, 1045 (1934); (b) deuterium, H. L. Johnson and E. A. Long, J. Chem. Phys. **2**, 389 (1934); (c) nitrogen and carbon monoxide, C. O. Davis and H. L. Johnson, J. Am. Chem. Soc. **56**, 271 (1934); (d) oxygen, H. L. Johnson and M. K. Walker, *ibid.* **55**, 172 (1933).

[11] J. K. Roberts, Proc. Roy. Soc. **A129**, 146 (1930); **A135**, 192 (1932); **A142**, 519 (1933). W. B. Mann, *ibid.* **A146**, 776 (1934). W. B. Mann and W. C. Newell, *ibid.* **A158**, 397 (1937). B. Raines, Phys. Rev. **56**, 691 (1939).

percent in the tabulated mean values of the accommodation coefficients. The important function of the parenthetical entries is to emphasize the fact that the useful pressure range for determining accommodation coefficients on gas covered wire by the present method will in every case be limited by the necessity of having pressures high enough to insure surface saturation of the wire and at the same time low enough to insure complete free molecule conduction.

The values of Table I, particularly those for helium, show that, within the experimental error, the mean accommodation coefficient for each of the gases may be considered as constant in the temperature interval 19°–30.5°C.

The recent results of Thomas and Olmer have already been mentioned in connection with the necessity for extending measurements into the pressure range which insures surface saturation of the wire. In the calculation of their accommodation coefficient values they seem to have made an error which, together with their use of pressures below 0.05 mm, renders meaningless any comparison between their values and those of Table I. In their experiments the wall of the gauge was thermostated at 30°C and accommodation coefficients determined at a series of wire temperatures extending, in some cases, to about 400°C. For each gas they obtain a value for the accommodation coefficient at 30°C by extrapolation to zero temperature difference between wire and wall. Unfortunately, in their expression for the quantity of energy removed per second at unit pressure by free molecule conduction they use the absolute temperature of the wall, 303°K, instead of the absolute average temperature of the gas. This is equivalent to assuming that the gas which conducts heat from the wire to the wall has a density characteristic of the wall temperature rather than the average temperature between wire and wall. It has been previously pointed out that this average temperature is a function of the accommodation coefficient on the wire (when the accommodation coefficient on the wall may be taken as unity), the wire temperature, and the wall temperature. Using the accommodation coefficients reported by Thomas and Olmer, the average absolute temperature of the gas when the wire is at 330°C is 334°K for hydrogen ($a=0.22$) and 415°K for mercury ($a=1.00$). For gases with intermediate accommodation coefficients the average absolute gas temperature will lie between these values for the same temperature difference between wire and wall. Although the square root of the average absolute temperature appears in the free molecule conduction expression, the high temperature differences existing in the apparatus of Thomas and Olmer may result in serious errors when the accommodation coefficients are computed using incorrect values for the average absolute temperature of the gas. For example, the accommodation coefficient of mercury derived from measurements with a wire temperature of 330°C should be multiplied by $(415/303)^{\frac{1}{2}}$. In general all the accommodation coefficients of Thomas and Olmer calculated from experimental measurements are low, the magnitude of the error increasing with the temperature difference between wire and wall.

The features of the present method of measuring accommodation coefficients which are of particular importance may be summarized as follows.

By limiting the average temperature difference between the wire and walls to about 2°, it is possible to assume that the total emissivity and the thermal conductivity of the platinum are constant over the wire length and that the rate of energy loss by radiation is proportional to $T_0^3\Delta t$ without affecting by more than 0.1 percent any single accommodation coefficient in the useful pressure range. By including in the Wheatstone network a compensator in thermal contact with the gauge walls it is possible to keep practically constant the average temperature difference between the wire and walls at bridge balance. For example, when the wall temperature changes from 18.9° to 30.5°C, the average temperature difference between the wire and walls changes by only 4 percent, from 2.060° to 2.148°. Moreover, in any given case the magnitude of this small change can be exactly calculated. Finally, by confining the platinum wire between parallel plates only $\frac{1}{8}$ inch apart, it is possible to use pressures sufficiently high (while still maintaining complete free molecule conduction) to insure that the resulting accommodation coefficients refer to a gas saturated wire and not to a wire on which the extent of adsorption is unknown.

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Molecular Constants and Chemical Theories*

I. The Parachor (Molecular Volume)

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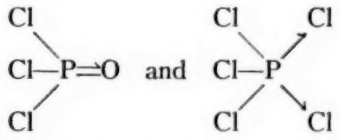
Theories of valency are based on physical properties of molecules, most of which are expressed in terms of so-called "additive molecular constants." Dipole moments, molecular volumes, bond distance, energies of formation, etc., belong to this class. The following paper intends to show that such constants are capable of being consistently interpreted in various entirely different ways. Hence a number of entirely equivalent but different and discordant theories of valency are possible, leading, for instance, to classical or to resonance structures of inorganic molecules. The choice between them therefore is arbitrary and not due to necessity. In the following part, I, one of these additive molecular constants, namely, the molecular volume in terms of the parachor, is studied in detail. The existence of coordinate types of covalent linkage having been ruled out by new experimental evidence for many inorganic first-order molecules formed by a definite central atom (Section 1), a new set of atomic parachors is calculated on the basis of the classical formulae of chemistry (Section 2). Instead of resorting to different types of bonds and their respective parachor constants, it ascribes different constants to the same atom in different valence states (Section 3). The contributions of the constituent atoms to the volume of the covalent molecule thus calculated bear a close relation to their atomic numbers and to their ionization potentials (Section 4). The new atomic parachors account for such molecules as N_2, O_2, N_2O, CO, CO_2, SO_2, which earlier had to be considered as anomalous, and also give the correct structure of the azides. However, as the molecular volume apparently can be separated into atomic contributions according to entirely different concepts of valency, the parachor (i.e., the molecular volume) is an example of an additive molecular constant which is unable to distinguish between different possible structures of a molecule or the different conflicting chemical theories on which they are based.

1. INTRODUCTION

THE parachor was originally introduced by Sugden[1] as an additive and constitutive molecular constant which permits a comparison of atomic and molecular volumes in a convenient way. As with other similar molecular constants it was found soon not to lead to strictly additive operations but to be influenced by a number of constitutive factors as well. In particular, the molecular parachor of a molecule such as PCl_3 having been separated into contributions of the constituent atoms, it is not possible to reconstruct the molecular parachor of a molecule like PCl_5 or $POCl_3$ by adding up these atomic parachors. This happens whenever atomic parachors are calculated from a molecule formed by a central atom in its lower state of valency, and are applied to another one the central atom of which is in a higher valence state. Consequently these differences have been ascribed by Sugden to differences of linkage, such molecules having been formulated as



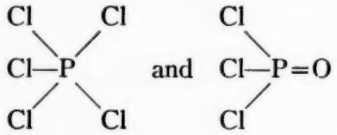
with semipolar double bonds and singlet linkages.* This interpretation of the parachor has at times greatly contributed to the acceptance of these types of linkages into chemical theories. Its influence can still be felt in those wave mechanical theories of valency in which these types of linkages are represented as enhanced resonance of covalent and ionic parent structures.

* The following paper in both its parts originates in a course of lectures on "chemical physics" which the author delivered last winter as visiting professor of The Illinois Institute of Technology. In the chapter on additive molecular constants, some of these were recalculated in order to compare their working and interdependence from the viewpoint of a uniform concept of chemical linkage. Some of the results are communicated here.

[1] S. Sugden, *The Parachor and Valency* (London, 1930), and references therein.

* The half-barb symbols ⇌ and ⇀ are used throughout this paper to indicate semipolar double bonds and singlet linkages, respectively, while the arrow → is retained for dipole moments. Sugden's symbol [P] is occasionally used for parachor values. The parachor is defined by $[P]=MT^{\frac{1}{4}}/D-d$ (M=mol. weight, T=surface tension, D and d=the densities of liquid and vapor phase, respectively). Comparison of [P] values of different molecules amount to a comparison of molecular volumes at constant surface tension.

However, an entirely different interpretation of this constant is also possible. In the above example the atomic parachor of phosphorus is kept constant and variations are introduced for the bond. Instead, the bond constants may be kept constant and different parachors used for phosphorus in its tri- and pentavalent state. Such a procedure is common practice for molecular refractivities, and Hunter and Samuel[2] have shown that a similar system of atomic parachors may be developed in which exactly the same additivity obtains.* This procedure of course leads directly to the older structural formulae like



which do not recognize different varieties of the non-electrostatic bond. The authors confined themselves to a few examples of typical molecules, as at that time they merely wished to show that the parachor does not provide diagnostic information as to different varieties of covalent linkages.

Precisely for this type of molecules formed by a marked central atom which may exist in two or more different states of valency, Sutton and his collaborators[3] have recently provided the final argument. The bond moments such as P→O, P→S, or S→O taken in conjunction with atomic distances from electron diffraction measurements are by far too small for semipolar double bonds, and they conclude that ordinary double bonds have to be reintroduced for such structures.** As has been shown earlier[4] in reality there does not exist a sufficient experimental basis for the concept of coordinate bonds for molecules of this type and spectroscopical results appear to be incompatible with it. These new results directly disclose the absence of such bonds in the most typical molecules. At the same time, as Sugden's system of atomic parachor constants is workable only with this difference of linkage, this new experimental evidence deprives it of its physical basis.

As this is the situation, two avenues of investigation suggest themselves for obvious reasons. Provided comparison of atomic and molecular volumes by means of the parachor (i.e., the molecular volume) are not to be abandoned entirely as a source of information on molecular structures, the alternative system of interpretation workable without resort to semipolar double bonds has to be fully developed. Secondly, the empirical and theoretical evidence has to be examined with a view to determining whether the results of such a procedure are compatible with conclusions on molecular structures reached in related fields.

In Part I of this communication, new additive values for atomic parachor are calculated under the assumption of different values for different valence states of the same atom but with only one variety of covalent linkage. An entirely consistent system results which, however, can be based only on the classical structural formulae of chemistry. In this first part they are taken for granted, including the pentacovalency of nitrogen, as the only means left to obtain additivity of the atomic parachors, i.e., the contribution of the constituent atoms towards the volume of the molecule. The more detailed study of the parachor, however, should be considered as a model only. In a shorter review of other molecular constants such as dipole moments, bond energies, or bond distances, it will be shown in Part II that similar systems of additive constants based on the classical structures, are entirely workable for all of them. For molecules (of Werner's first order) formed by a definite central atom, the older classical formulae including pentacovalency of nitrogen, will be seen to be entirely compatible with the wave mechanical representation of valency. The contributions of ionic parent structures will emerge as much smaller than sometimes thought, and of the same order for ordinary covalent as well as for the so-called coordinate bonds. From the very definite result that any additive molecular constant may be separated

[2] R. F. Hunter and R. Samuel, Rec. Trav. Chim. **54**, 114 (1935); Chem. and Ind. **54**, 31, 467, 635 (1935).

* Conversely, it is entirely possible to rewrite the theory of molecular refractivities with one constant only per atom and different constants for the bonds.

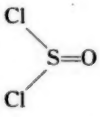
[3] L. E. Sutton, Ann. Repts. **37**, 74 ff. (1940) and references therein.

** Difficulties inherent in the calculation of bond moments may render this conclusion not entirely inevitable in some cases, yet it certainly holds for a molecule such as SO_2; cf. Part II of this paper.

[4] R. F. Hunter and R. Samuel, Nature **138**, 411 (1936) and references therein.

into additive atomic increments according to different systems of structures and according to different chemical concepts, one definite conclusion can be drawn, namely, that none of them is able to distinguish between different chemical theories. This reduces the experimental basis for some of them, and therefore it becomes quite likely that the classical structures, taken for granted in Part I, indeed are the nearest approach to reality.

TABLE I. Calculation of atomic parachors.*
(The superscripts indicate the state of valency in covalent linkage, not an ionic charge.)

Molecule	Molecular parachor	Atomic symbol	Atomic parachor	Remarks
1. $(C_2H_5)_2O$	211.7 209.5	—O—	20.5	*
2. O=C=O	77.5	=O	36.4	*
3. C=O	61.6	C^2	28.4	*
4. S=C=S	144.1	$=S^2$	69.7	*
5. C_2H_5—S—H	257.5 256.4	$—S^2—$	49.8	
6. 	174.5	S^4	29.5	*
7.	195.3	S^6	13.9	*
8. S=C=Se	156.4	$=Se^2$	81.9	
9. $(C_6H_5)_2Se$	445.6	$—Se^2—$	65.6	
10. $(C_6H_5)_2SeO$	461.6	Se^4	45.2	
11. $(C_6H_5)_2Te$	457.4	$—Te^2—$	77.4	
12. $(Et\cdot O\cdot C_6H_4)_2Te_2$	723.0	$=Te^2$	87.7	
13. $(C_6H_5)_2TeCl_2$	547.3	Te^4	58.7	
14. NOCl	108.1	$>N^3—$	17.4	**
15. $(C_6H_5)—N^3=N^5\equiv N^3$	267.3	$=N^3—$	32.6	
16. N≡N	60.4	$\equiv N^3$	43.0	
17. $(C_6H_5)NO_2$	264.5	N^5	1.7	
18. PCl_3	201.1 199.0	P^3	37.1	
19. $Cl_3P=O$	217.6	P^5	18.3	
20. $SbCl_5$	311.8	Sb^5	40.3	
21. $SnCl_2$	183.8	Sn^2	75.2	
22. $PbCl_2$	194.5	Pb^2	85.9	

* Similar values used already by Hunter and Samuel, reference 2.
** N is the positive partner and the constant of the double bond therefore included in the increment of oxygen. Values derived from amines are similar but show slight variations.

2. CALCULATION OF ATOMIC PARACHORS

The results of a calculation of atomic parachors are listed in Table I. They are the contributions made by the individual atoms to the parachor of a covalent molecule. The separation of molecular into atomic parachors is then confirmed or justified by Table II, in which the observed parachors of a number of typical molecules are compared with those calculated by means of the new values of Table I as well as with those calculated according to Sugden's method.

Table I is almost self-explanatory, and only a few remarks on some details of the calculations are necessary. The values of C and H calculated by Sugden from the increase of the parachor per CH_2 group in various homologous series can be accepted as the basis for any separation of molecular parachors into contributions of the constituent atoms. In the same way the proposed change in the method of calculation cannot affect such of Sugden's values as are derived from those of C and H directly and by means of simple structural formulae. These include the halogen atoms (from simple aliphatic compounds), the tetravalent atoms of the fourth group based on measurements of the tetrahydrides of Si, Ge, Sn, and Pb,[5] respectively, and those of the trivalent atoms As, Sb, Bi, and B, taken from halogenides MX_3. They are included in Table III.

For the increase of the parachor produced by a double or triple bond, we accept Sugden's value as far as the C atom is concerned, i.e., the atomic parachors of 4.8 for >C<, 4.8+23.2=28.0 for >C=, and 4.8+46.6=51.4 for —C≡.*

However, the increase per double bond changes with different atoms, and Sugden introduced already a special value for the carboxyl group. In the present system no attempt has been made to

[5] Corrected values of D. T. Lewis, J. Chem. Soc., p. 1056 (1938).

* Sugden's increment of 46.6 for the triple bond is an average for substances containing both the groups —C≡C— and —C≡N. For the former the empirical value appears to be lower, i.e., 44.8 in HC ⋮ CH or 40.1 in $CH_3\cdot C$ ⋮ CH, and for the CN group it will be lowered by the new and slightly higher parachor of N. Hence the final value will be rather nearer 44 than 47.—The value of 23.2 for the carbon double bond will also be used for divalent carbon in isocyanides. Small improvements of additivity might be obtained in these two directions, as also for O in carbonyl and carboxyl groups.

TABLE II. Observed and calculated molecular parachor.

Substance	[P] observed	New calculation [P] calculated	Formula used	Calculation after Sugden [P] calculated	Formula used
A. Sulphur compounds					
1. Sulphur dioxide	101.5	102.3	$O{=}S^{4}{=}O$	109.8	$O{=}S{\rightarrow}O$
2. Sulphur chloride	204.3	205.6	$S^{2}{=}S^{4}$ (Cl, Cl)	205.0	$S{=}S$ (Cl, Cl)
3. Ethyl sulphite	299.7	297.1	$(EtO)_2S^{4}{=}O$	298.4	$(EtO)_2S{\rightarrow}O$
4. Ethyl toluene sulphinate	410.3	410.5	C_7H_7, $S^{4}{=}O$, EtO	410.7	C_7H_7, $S{\rightarrow}O$, EtO
5. Ethyl ethane sulphonate	295.8	297.4	EtO, O, S^{6}, O, Et, O	298.4	OEt, $O{=}S{\rightarrow}O$, Et
6. Methyl sulphate	238.9	239.9	MeO, O, S^{6}, O, MeO, O	240.2	OMe, $O{=}S{\rightarrow}O$, OMe
7. Diphenyl sulphone	465.7	466.9	Ph, O, S^{6}, O, Ph, O	465.1	Ph, $O{=}S{\rightarrow}O$, Ph
8. Methyl toluyl sulphone	369.8	370.2	C_7H_7, O, S^{6}, O, Me, O	370.2	C_7H_7, $O{=}S{\rightarrow}O$, Me
9. Ethyl toluene sulphonate	431.8	431.3	C_7H_7, O, S, O, EtO, O	429.2	C_7H_7, $O{=}S{\rightarrow}O$, OEt
10. Toluene sulphonyl chloride	367.8	370.0	(C_7H_7), O, S^{6}, O, Cl, O	368.4	C_7H_7, $O{=}S{\rightarrow}O$, Cl
11. *Sulphuric acid— from to	144.8 152.3	150.3	H—O, O, S^{6}, O, H—O, O	147.6	O—H, $O{=}O{\rightarrow}O$, O—H
B. Selenium and tellurium compounds					
12. Phenyl selenium bromide	321.4	323.6	$Ph{-}Se^{2}{-}Br$	320.5	Ph—Se—Br
13. Diphenyl diselenide	506.5	510.2	$Ph{-}Se^{2}{-}Se^{2}{-}Ph$	505.0	Ph—Se—Se—Ph
			or		
	506.5	507.1	Ph, $Se^{4}{=}Se^{2}$, Ph		

* Calculated with Mumford and Phillips value of 11.3 for H in OH. Cf. reference 6.

TABLE II.—*Continued.*

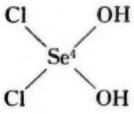
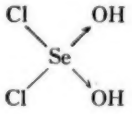
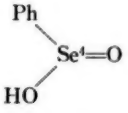
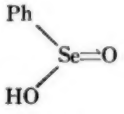
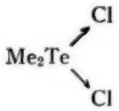
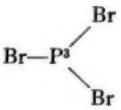
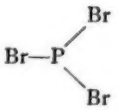
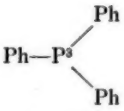
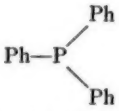
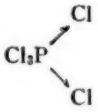
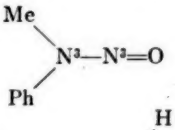
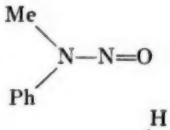
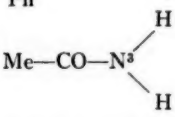
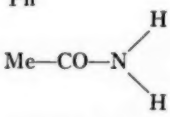
Substance	New calculation [P] observed	[P] calculated	Formula used	Calculation after Sugden [P] calculated	Formula used
14. Selenium oxychloride	181.1	190.2	$Cl_2{=}Se^4{=}O$	189.5	$Cl_2{=}Se{\rightarrow}O$
15. *Selenium oxychloride hydrate	222.8	217.4		208.9	
16. *Phenyl selenious acid	299.5	303.4		302.2	
17. Dibutyl telluride	426.8	430.0	$(C_4H_9)_2Te^2$	425.6	$(C_4H_9)_2Te$
18. Dimethyl tellurous dichloride	282.5	279.5	$Me_2Te^4Cl_2$	275.4	
C. Phosphorus compounds					
19. Phosphorus tribromide	242.9	241.1		241.7	
20. Triphenyl phosphine	607.7	607.1		607.7	
21. Phenyl phosphate	686.5	686.2	$(PhO)_3P^5{=}O$	686.1	$(PhO)_3P{\rightarrow}O$
22. Ethyl phosphate	399.1	401.5	$(EtO)_3P^5{=}O$	401.4	$(EtO)_3P{\rightarrow}O$
23. Phosphorus pentachloride	282.5	289.8		284.0	
D. Compounds of trivalent nitrogen					
24. Dimethyl nitrosamine	183.4	183.4	$Me_2{=}N^3{-}N^3{=}O$	180.4	$Me_2{=}N{-}N{=}O$
25. Diethyl nitrosamine	260.3	261.4	$Et_2{=}N^3{-}N^3{=}O$	258.4	$Et_2{=}N{-}N{=}O$
26. Methyl phenyl nitrosamine	313.6	317.3		314.6	
27. Acetamide	148.0	148.9		150.8	
28. Butyl nitrite	251.8	247.4	$C_4H_9{-}O{-}N^3{=}O$	248.8	$C_4H_9{-}O{-}N{=}O$
29. Amyl nitrite	287.4	286.4	$C_5H_{11}{-}O{-}N^3{=}O$	287.8	$C_5H_{11}{-}O{-}N{=}O$
30. Ethyl isothiocyanate	211.7	210.2	$Et{-}N^3{=}C{=}S$	207.2	$Et{-}N{=}C{=}S$
31. Phenyl isothiocyanate	304.8	305.1	$Ph{-}N^3{=}C{=}S$	301.9	$Ph{-}N{=}C{=}S$
32. Aceto nitrile	122.2	122.3	$CH_3{-}C{\equiv}N^3$	120.0	$CH_3{-}C{\equiv}N$

TABLE II.—*Continued.*

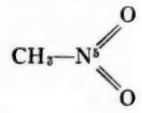
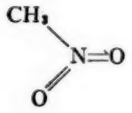
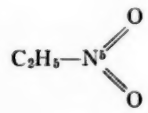
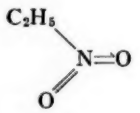
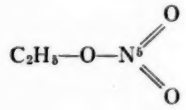
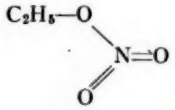
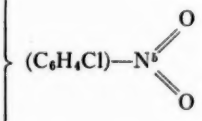
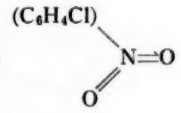
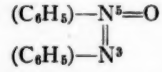
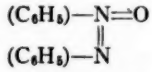
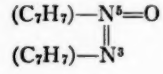
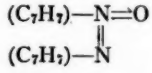
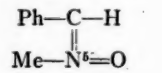
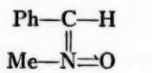
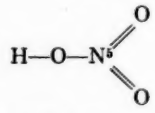
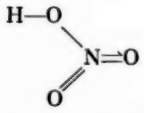
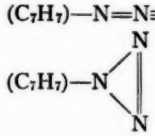
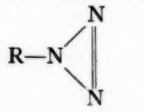
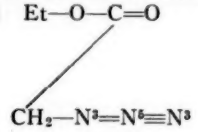
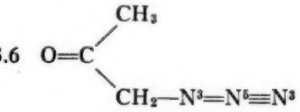
Substance	[P] observed	New calculation [P] calculated	New calculation Formula used	Calculation after Sugden [P] calculated	Calculation after Sugden Formula used
33. Hydrogen cyanide	81.5	83.3	$H—C\equiv N^{3}$	81.0	H—C≡N
34. Ethyl thiocyanate	210.7 209.1	211.1	$C_2H_5—S—C\equiv N^{3}$	207.2	$C_2H_5—S—C\equiv N$
35. Methyl isocyanide	122.1	125.1	$CH_3—N^{3}=C^{2}$	118.4	$CH_3—N\overset{\rightarrow}{\equiv}C$
36. Ethyl isocyanide	163.8	164.1	$C_2H_5—N^{3}=C^{2}$	157.4	$C_2H_5—N\overset{\rightarrow}{\equiv}C$
E. Compounds of pentavalent nitrogen					
37. Nitrous oxide	81.1	81.1	$N^{3}\equiv N^{5}=O$	89.8	$N\equiv N\rightarrow O$
38. Nitro methane	132.0	130.6		130.2	
39. Nitro ethane	171.2	169.6		169.2	
40. Ethyl nitrate	189.6	190.1		189.2	
41. o-Chloronitrobenzene	299.9	301.7		301.3	
42. m-Chloronitrobenzene	298.9	301.7		301.3	
43. p-Chloronitrobenzene	300.0	301.7		301.3	
44. Azoxybenzene	444.7	447.8		446.6	
45. o-Azoxy toluene	528.6	525.8		524.6	
46. Benzantialdoxime N-methyl	325.9	329.3		321.1	
47. *Nitric acid—					
from to	104.4 105.7	106.3		105.4	
48. p-Toluylazide	307.0	306.3	$(C_7H_7)—N^{3}=N^{5}\equiv N^{3}$	336.3	$(C_7H_7)—N=N\equiv N$, or
				306.4	
49. o-Toluylazide	303.8	306.3	$(C_7H_7)—N^{3}=N^{5}\equiv N^{3}$	336.3	$R—N=N\equiv N$, or
				306.4	

TABLE II.—*Continued.*

Substance	[P] observed	New calculation [P] calculated	Formula used	Calculation after Sugden [P] calculated	Formula used
50. Ethyl azido acetate	277.0	273.1		306.2	straight N_3 chain, or
				276.1	N_3—ring
51. Azido acetate	220.9	213.6		250.4	straight N_3 chain, or
				220.3	N_3—ring

maintain a constant value of the multiple bond but according to the precedent of atomic refractivities different values have been calculated for —O— and O=, —S— and S=, —Se— and Se=, —Te— and Te=, as well as for —N<, —N=, and N≡. Indeed, the many different values needed for molecular refractivities of nitrogen or sulphur compounds would suggest that the double-bond values themselves also would be affected by the state of valency of atoms, being different, e.g., in the nitro and the nitroso group. But additivity is already obtained if the >C= and —C≡ values are taken, as long as these atoms are concerned, and the respective multiple bond values for the *negative* atom in all other cases. This simple rule established one parachor value only for all atoms in higher states of valency, as they invariably act as the positive end of a dipole moment. All numerical values will be found in Table I.

Finally, all increments for the formation of rings can be taken over from Sugden's calculation and Mumford and Phillips' [6] value for hydrogen in the hydroxyl group, where it is about one-third lower. This is entirely analogous to conditions prevailing for molecular refractivities. It is the only case where a change of polarity makes itself perceptibly felt in parachor calculation, while similar conditions are often met with in molecular polarizibilities. On the other hand, the latter does not need special purely geometrical factors, e.g., for the formation of rings. Refractivities measure the polarizibility of the electron cloud and the parachor is essentially a measurement of volume. It is therefore not surprising that the former is more affected by factors of polarity, the latter more sensitive to geometrical influences.

The calculations of atomic parachors are now carried out in Table I. For molecular refractivity it has become customary not to use values from literature, but to measure refractive index and density of the same specimen. Sufficient measurements of this kind are not available for the parachor in all cases. We have therefore preferred to base the fundamental values on such molecules, which are simple in structure, easier to be purified in the liquid state, and do not possess an enhanced polarity which in some degree might lead to an ionic dissociation.

3. ATOMIC PARACHORS AND MOLECULAR STRUCTURES

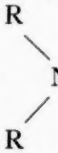
In Table II, observed molecular parachors of a number of typical molecules[7] are compared with those calculated in accordance with Sugden's method as well as the constants derived in Table I. Table II therefore provides justification for this subdivision into atomic parachors according to the state of valency, and also for the structural formulae in which no use is made of semipolar or singlet linkages or their counterpart of resonance structures. A still better agreement between calculated and observed parachors could be reached by taking for the atomic parachors the mean values from measurements of a number of similar molecules instead of one value only from one particular molecule and measurement.

[6] S. A. Mumford and J. W. C. Phillips, J. Chem. Soc., p. 2112 (1929).

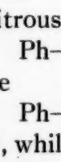
[7] Besides the experimental values collected by Sugden, reference 1, those of D. L. Hammick, R. C. A. New, N. V. Sidgwick, and L. E. Sutton, J. Chem. Soc., p. 1876 (1930) have been used for the isocyanides.

The constants of Table I are still unnecessarily afflicted by fortuitous experimental errors. However, this method of comparison suggested itself as better suited for the present purpose which is to demonstrate that the division of molecular parachors into atomic constants according to the state of valency rather than according to different kinds of covalent linkage, is entirely workable.

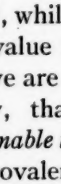
It will be seen that the newly calculated values are as good as the old ones, and in general there is little to choose between them. All through the old structural formulae have been used. Indeed, it is very gratifying to observe the almost automatic working of these formulae. To mention just one instance. The parachor value of a N_2 group is fully represented* by N^3+N^3 in the



nitrosamines N—N=O (Nos. 24, 25, 26), as



N^3+N^5 in nitrous oxide N≡N=O (No. 37), in



azoxybenzene and similar molecules (Nos. 44, 45), while the azide group —N=N≡N obtains its value from $2N^3 + 1N^5$ (Nos. 48 to 51). Hence we are now in a position definitely to state, firstly, that if they should exist, *the parachor is unable to distinguish* between different varieties of covalent linkage, and, secondly, that these classical structures which recognize only one kind of covalent bond, *are entirely sufficient for the representation of such additive molecular constants* as the parachor or molecular refractivities.

TABLE III. Atomic parachors and periodic table.

H 17.1 He 20.5									
Be	(22.8)								
B	15.9								
>C<	4.8	Si^4	28.7	Ge^4	40.1	Sn^4	57.9	Pb^4	75.0
C^2	28.0					Sn^2	(75)	Pb^2	(86)
N^5	1.7	P^5	18.3			Sb^5	(40)		
N^3	17.4	P^3	37.1	As^3	50.3	Sb^3	66.0	Bi^3	(~80)
		S^6	13.9						
		S^4	29.5	Se^4	45.2	Te^4	58.7		
O<	20.5	S^2	49.8	Se^2	65.6	Te^2	77.4		
F	(25)	Cl	54.3	Br	68.0	I	91.0		
Ne	25	Ar	54						

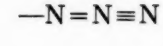
Attention may now be drawn to some details of Table II, and first of all to those molecules the parachor of which has not been explained before. These simple molecules with "anomalous" parachor are listed by Sugden[1] as N_2, O_2, N_2O, CO, CO_2, SO_2, and SO_3. We have not been able to calculate $[P](SO_3)$ satisfactorily, and as it is the only one which is left, the experimental value might not be entirely reliable. Most of the other molecules are already included in Tables I and II. (Cf. Table I, Nos. 2, 3, 16; Table II, Nos. 1 and 37.) Thus CO has been used to calculate $[P](C^2)$, and the same value of C^2 has been checked by the calculation of the isocyanides. From CO_2 we took the value of O=, verified by numerous other molecules containing a double bonded O atom. The N_2 molecule was used to calculate the value of the triple bond between N and N, and the same value for N≡ then occurs again in the azide group —N=N≡N. Finally, $[P](N_2O) = 81.1$ (obs.) can be calculated according to N^3+N^5+O or $43.0+1.7+36.4 = 81.1$. The parachor for oxygen, O_2, has been observed as 54.0. This value is fully represented by adding the parachors of two O atoms plus one oxygen-double bond, or $[P](—O—)+[P](O=) = 20.5+36.4 = 56.9$.

The disappearance of anomalous parachors to our mind presents intrinsic evidence for this method of subdivision approaching nearer to reality.

Another type of molecule, where the present method has a decided advantage over the old one, is that formed by the azide group. The two methods give these values of the parachor of the possible configurations

I

II



$[P]$ (Sugden)	77.4	107.3,
$[P]$ (pres. method):	84.6	77.3;

observed: $[P]\,N_3 = 77.2$.

The observed mean value $[P](N_3)$ of 5 azoimides is 77.2. Consequently, Sugden had to

* Superscripts mark the state of valency, not the charge.

ascribe the ring structure to the azide group, while the open chain would be preferred for the present calculation. In the meantime electron diffraction measurements[8] have shown that methyl azide possesses the open chain structure (with a valency angle CNN = 120°). Even on the basis of the resonance interpretation of coordinate bonds there is hardly a possibility open to change this result, because the observed dipole moment and interatomic distances agree too well with those calculated on the basis of the classical formula II. This will be shown in Part II (Section 3) of this paper.

4. ATOMIC PARACHOR AND ATOMIC NUMBER

In Table III and in Fig. 1 the parachors of atoms are collected according to their position in the periodic table.*

The following conclusions suggest themselves immediately:

(1) In a column of the periodic table, i.e., proceeding from C to Pb, N to Bi, O to Te, and F to I, the atomic parachors increase regularly with the main quantum number, as they ought to do if the parachor measures the atomic volume in covalent linkage. This is also true for different states of valency.

(2) The atomic volume of the same atom in a lower state of valency is always larger than in a higher state. Indeed, the transition from C^2 to C^4, N^3 to N^5, etc., always implies the activation of two more electrons (in most cases the outside s^2 electrons, but a $\pi(p)$ pair in such atoms as S^4). While on an atomic orbital in the lower state, they are changed to a molecular orbital in the higher one. Here they partly belong to the other atom, and while increasing the volume of the latter, they decrease that of the former. It will be seen that the lowest parachors are with those atoms like N^5 which can only be the positive partner of any combination, the largest with those like S^2 or Cl^1 which most frequently form the negative partner.* In other words, the volume taken up by a particular atom in a covalent molecule largely depends on the shift of the electrons from it or towards it. This appears to agree well with the calculation of Lennard-Jones and Corner,[9] in which the molecular parachor is a function of the attractive and repulsive intermolecular potentials.

(3) A multiple bond always increases the atomic parachor. For the parachor as a function of the molecular volume this is by no means an obvious result because the covalent radii[10] are shortened by the multiple bond. As electron diffraction and x-rays in the main measure the position of the nuclei, and as also the atomic refractions are increased by multiple bonds, the increase of volume has again to be attributed to the binding electrons. This effect, which could be pictured as a kind of spreading of the electrons in space, is of course connected with directions of the bonding orbitals.

(4) In comparing the atomic parachors in the same period, i.e., from Be to F and Ne, etc., the change of atomic volume appears to be regulated by the ionization potential. The following points suggest themselves: (a) In the series Be^2, B^3, C^4, N^5, and similarly for Si^4, P^5, S^6, in which all the valence electrons are chemically active, the atomic volume steadily becomes contracted with increasing nuclear charge. (b) The same is true for C^2 and N^3, P^3, and S^4, or the series Sn^2, Sb^3, Te^4, for which the nucleus is always screened by the same number of electrons (in these atoms the two outside s electrons). (c) Conditions are different for a series of atoms like C^4, N^3, O^2, F^1, Ne, or Si^4, P^3, S^2, Cl^1, and Ar. Here the nuclear

[8] L. Pauling and L. O. Brockway, J. Am. Chem. Soc. **59**, 13 (1937).

* Some of them are not yet certain. Those of Sn^2, Pb^2, and Sb^5 cannot be checked for lack of experimental data, and the chlorides from which they are calculated are near to the limit of electrovalent linkage. Some fraction might already be dissociated into ions according to the varying experimental conditions. Those for some metals, particularly Be, have to be taken from chelated compounds in which the organic radicals form rings [cf. N. V. Sidgwick, *The Electronic Theory of Valency* (The Clarendon Press, Oxford, 1927)]. To our mind, this is due only to enhanced dipole forces between Be and the double-bonded oxygen atom (cf. references 2 and 4). It is therefore difficult to decide whether this ring has to be recognized as a co-volume and an increment for ring formation is to be included in the calculation. In that case the atomic parachor of Be from its acetyl acetonate comes to 10.6, without the ring constant to 22.8. The latter figure has been tentatively adopted, mainly because the covalent radii [see L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, 1939), p. 154] decrease as Be > B > C > N.

* This point is brought out still more clearly in the system of atomic refractivities, where it is easy to distinguish between, say, P in PH_3 and in PCl_3. The numerical values are $P^{3-} = 8.54 > P^{3+} = 6.55$ (cf. reference 12).

[9] J. E. Lennard-Jones and J. Corner, Trans. Faraday Soc. **36**, 1156 (1940).

[10] Cf. L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, 1939), p. 154.

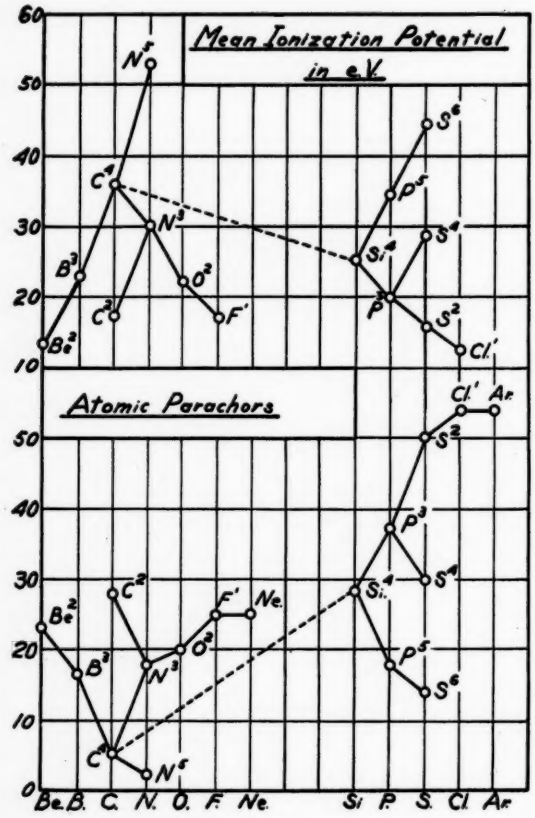


FIG. 1. Covalent parachors and mean ionization potentials of atoms.

charge and the number of electrons increase step by step, but less and less take part in the chemical bond. Hence the volume contributed to that of the covalent molecule by the reference atom increases more and more, obviously converging to the numerical value of the free rare gas atom, which follows.

This behavior suggests the strength of the nuclear field as the main factor on which the parachor depends, and in order to test this concept the mean ionization potential per valence has been added in Fig. 1. This quantity has been introduced earlier[11] as a convenient means to follow the transition from covalent to electrovalent linkage. It is the arithmetic mean for all the ionization potentials relevant to the particular state of valency, e.g., the mean of the first, second, and third ionization potential of N for N^3, that of the first to fifth for N^5.

As will be seen at once, the two curves of atomic parachors and mean ionization potential have the general character of mirror images. In other words, the higher the mean ionization potential, the more the electron cloud is contracted and hence the smaller the volume contributed by the particular atom to that of a covalent molecule.

Finally, a comparison of the atomic parachors with atomic refractivities suggests itself. The latter ones are understood to be the contributions of the individual atoms to the polarizibilities of *covalent* molecules. Attempts have been made to

[11] R. Samuel and L. Lorenz, Zeits. f. Physik **59**, 53 (1929); R. F. Hunter and R. Samuel, Chem. and Ind. **55**, 733 (1936).

TABLE IV. Atomic refractivities in covalent inorganic molecules (for *D* lines).
(Superscipts indicate the state of valency in polar covalent linkages, but not ionic charges.)

H 1.04 (H^+ 0.98)				
He 0.50				
B 3.51				
>C< 2.42	>Si< 4.87	>Ge^4< 8.34	>Sn^4< 11.24	>Pb^4< 13
C^2 2.93				
N^{5+} 2.52	P^{5+} 6.55			
N^{3+} 3.90	P^{3+} 8.54			
>N^{3-}— 2.3, ≡ N^{3-} 3.07	P^{3-} 8.65			
	S^{6+} 2.99	Se^{6+} 4.66	Te^{6+} 6.10	
	S^{4+} 6.19	Se^{4+} 11.1		
—O— 1.64, O=2.21	S^{2+} 7.5, S^{2-} 8.31			
—O′ 4.06				
(O″~7)				
	Cl^{7+} 2.63			
F^- 1.45	Cl^- 5.82	Br^- 8.72	I^- 16.02	
Ne 1.00	Ar 4.20			

establish additive values of refractivities for inorganic molecules which would reduce the great number of empirical constants used for calculations of molecular refractivities, but none has entirely succeeded for a number of reasons. These are partly of theoretical, partly of experimental nature. For instance, even disregarding variations of polarity, the average value of the polarizibility α should be split according to the various axes of the molecule and α extrapolated to infinite wave-length, in order to obtain strict additivity. At the same time, all such molecules would have to be discounted, for which the reference wave-length of measurement is too near to their first absorption band and already for such simple molecules as Cl_2, HBr, CS_2 this condition hardly holds.

However, even without strict additivity, reasonable constant values of atomic polarizibilities may be calculated, and it is of some theoretical interest to show the existence of a near relationship with the atomic parachors, although the two constants are obtained in such entirely different ways. For the sake of convenience only, a set of figures published earlier[12]

TABLE V. Molecular refractivities (D lines).

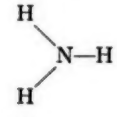
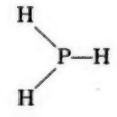
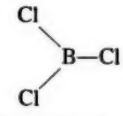
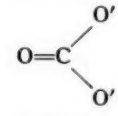
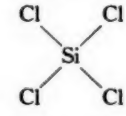
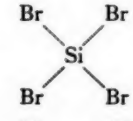
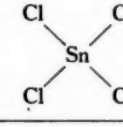
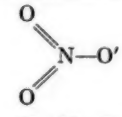
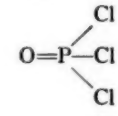
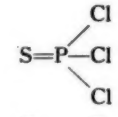
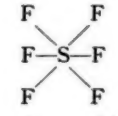
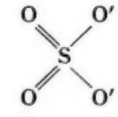
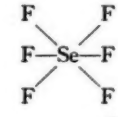
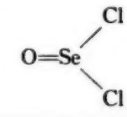
Molecule	Formula used	Mol. refractivity calc.	obs.
HCl	H—Cl	6.86	6.67
H_2O	H—O—H	3.72	3.76
NH_3		5.33	5.61
PH_3		11.72	11.68
BCl_3		20.97	20.97
CO_2	O=C=O	6.84	6.68
$[CO_3]''$		12.18	12.27
CS_2	S=C=S	22.50	22.13
$SiCl_4$		28.15	28.15
$SiBr_4$		39.65	40.85
$SnCl_4$		34.52	34.52

TABLE V.—*Continued.*

Molecule	Formula used	Mol. refractivity calc.	obs.
$[NO_3]'$		11.00	11.00
N_2O	N≡N=O	7.80	7.31
$POCl_3$		26.22	25.13
$PSCl_3$		32.8	32.65
SF_6		11.67	11.69
$[SO_4]''$		14.39	14.63
SeF_6		13.36	13.36
$SeOCl_2$		25.0	25.0

[12] R. Samuel, Zeits. f. Physik **49**, 95 (1928). The value for the contribution of oxygen with one covalent and one electrovalent link to a molecule such as $[NO_3]^-$ has been derived under certain assumptions which would not be made today. They are not necessary, as this value could be taken directly, e.g., by comparing CO_2 and $[CO_3]^{2-}$. The refractivities of $PSCl_3$ and $SeOCl_2$ have been added and that of $POCl_3$ has been changed according to the paper of C. P. Smyth, G. L. Lewis, A. J. Grossman, and F. B. Jennings, J. Am. Chem. Soc. **62**, 1219 (1940). The symbol R (X) is used to indicate the molecular or atomic refractivity of the molecule or atom X.

is used here (Table IV) and comparison of calculated and observed data (Table V) shows, that they are sufficiently accurate and additive to indicate the relation of atomic polarizibilities and atomic number in simple covalent inorganic molecules.

It will be seen (1) that different values obtain for different states of valency, e.g., $R(S^6) = 2.99$, $R(S^4) = 6.19$. That of the higher one is always smaller, i.e., the chemically inactive electrons follow more easily the outside field.

(2) Separate values for the same atom in the same valence state are necessary, according to its being the positive or the negative partner of the combination. Obviously the polarizibility is more sensitive to polarity of the bond than the parachor, where such a condition prevailed only for hydrogen in the —OH group.

(3) The multiple bond always increases the polarizibility.

(4) The polarizibility of atoms in covalent linkage increases in a column of the periodic table, e.g., from F to Cl or C to Pb exactly as the parachor (and also as Fajans' refractivities of free ions).

(5) The polarizibility of an atom in covalent linkage is larger than that of its positive and smaller than that of its negative ion; the former possesses less electrons than the atoms and these are held in a field of excessive positive charge, while the latter possesses more electrons than the atom, in excess of its nuclear charge. This is clearly shown by the three values of oxygen. The first R(—O—) is that in organic molecules R—O—R, the second R (—O′) that contributed by one of them in an anion such as $[NO_3]'$, the third[13] that of the free ion O″. The parachors of positive and negative ions have been discussed by Mumford and Phillips[6] who in general find quite similar conditions.

(6) In a period, the atomic refractivities follow in general the reciprocal value of the (mean) ionization potential, as was to be expected.

The comparison of atomic parachors and atomic refractivities shows that both are similar in some respects, but vary in others. Thus stereometrical factors play a role in parachor calculations, to wit, the special increments for ring formation. Nothing similar is known for molecular refractivities. On the other hand, these are influenced so much more by the polarity of the bond that different values have to be introduced for the same atom as the positive or negative end of a dipole. Furthermore, the well-known "exaltations" of molecular refractivities in conjugated double bonds and similar structures indicate that the polarizibility is affected by the non-localization of the electrons, itself theoretically connected with the polarity of the molecules. This influence is sufficiently great to consider these exaltations as a measure of the mobility of these electrons, but no similar effect obtains for parachor values.

Apparently both depend, as stated above, on stereometrical as well as on polarity factors, but in different degrees. Refractivity, an induced dipole moment in the first instance, cannot be but affected by stereometrical arrangements within the molecule, e.g., a change in the length of the bond. The parachor is essentially a measurement of atomic volume, but, as said before, this itself depends on the cloud of electrons and their polarization therefore will have repercussions on the volume.

In order to estimate roughly the influence of these two kinds of factors on our two constants, they might be compared with other quantities known to represent one of these classes in particular. The length of the bond on the one side and the ionization potential on the other suggest themselves for such a purpose. However, as they run roughly anti-parallel in the periodic table, the one increasing from period to period, the other decreasing in the same sense, there is only one possibility left. On account of the difference in electronic structure in the preceding elements Ni, Pd, and Pt, the ionization potential runs irregular for the following atoms, e.g., for Cd it is lower than that of *both* its neighbors Zn and Hg. The covalent radius is hardly affected and the ionic radius not at all. Hence, in Fig. 2 atomic parachors and refractivities are compared with these constants. It will be seen that the depression of the mean ionization potential of Cd is reproduced in the enhanced polarizibility of Cd, as well for the free atom in the metallic vapor, as also for the atom in the covalent linkage of the diethyls. For the parachors, only values

[13] K. Fajans and G. Joos, Zeits. f. Physik **23**, 1 (1924).

for the free atom in the fused metallic state are available. Although not as entirely unaffected as the ionic radius, the curve follows much more closely that of the covalent radius than that of the ionization potential or the refractivities of the free atoms.

5. CONCLUSIONS

It has been shown that a system of additive atomic constants can be set up for the molecular volume, measured by Sugden's parachor, which is based on the classical structural formulae of chemistry. It is characterized by different constants for the same atom in different valence states, but does not resort to different constants for different types of covalent linkage.

It could be argued that any better agreement between observed and calculated values in this new representation is simply due to the greater number of independent constants. But in the older representation a number of molecules (anomalous parachors) could not be accounted for. They could find their place in the additive system only through the introduction of special constants, one for each molecule. As the present procedure takes care of these molecules automatically, the total number of additive constants has not really been increased.*

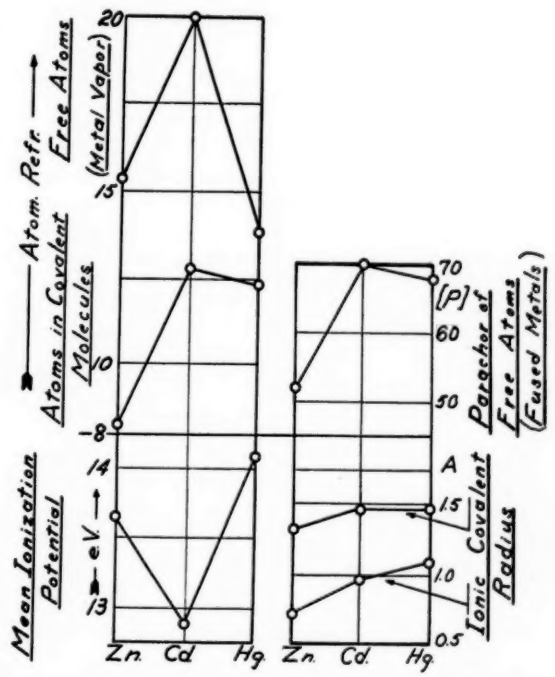


FIG. 2. Comparison of electrical and stereometrical factors.

On the other hand, the present system is superior to the older one in its correct representation of some molecules, e.g., the azides, and, most important of all, in conjunction with dipole moments, the new measurements of the bond distances have ruled out the application of constants for a coordinate link of all such standard molecules as SO_2, $SOCl_2$, $POCl_3$, etc. Hence there appears no other alternative left but to accept the present set of atomic constants.

The fact that such a separation of molecular into atomic parachors on the basis of the classical formulae is at all possible, makes it evident that the parachor is unable to distinguish between different equivalent structures or theories.

* For any additive molecular constant there remains indeed a third possibility of subdivision into additive contributions. Molecular refractivities, for instance, instead of being separated into atomic refractivities, also have been divided into bond refractivities. Rather than considering the contributions made to the polarization of a molecule by the electrons belonging to a particular atom, those of the electrons (of different atoms but) together forming a particular bond are examined. [A. L. V. Steiger, Ber. **54**, 1381 (1921); K. Fajans and C. A. Knorr, Chem. Zeits. **48**, 403 (1924); C. P. Smyth, Phil. Mag. **50**, 361 (1925); K. G. Denbigh, Trans. Faraday Soc. **36**, 936 (1940)]. As the dipole moments on account of their vector character have to be separated not into atom or group contributions but into bond moments, a comparison of the polarizibilities per bond has a good physical meaning. A distribution of the molecular parachors into bond parachors, however, appears not to serve a useful purpose and we have refrained from doing so. The number of constants to be used to achieve perfect additivity quite obviously is always the same, whatever method of subdivision is used.

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Molecular Constants and Chemical Theories

II. Additive Molecular Constants and Chemical Structures

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(Received December 27, 1943)

All additive molecular constants, besides parachor and molecular refractivities (Part I), in particular also dipole moments, bond distances, and energies of formation (or bond energies) may be separated into individual (atomic or bond) contributions according to different proposed structures of a covalent molecule or different chemical theories on which these structures are based. Such constants do not therefore possess diagnostic qualities as to the nature of different covalent bonds, and different theories or concepts based on them, by necessity are inconclusive. A number of standard examples of molecules formed by a marked central atom are considered, which often are assumed to establish the existence of a second variety of covalent linkage, i.e., coordinate bonds, or its wave mechanical counterpart, i.e., enhanced resonance of covalent and ionic (or other) forms. For all of them, all the above molecular constants are in perfect agreement also with the older classical formulae, including those of pentacovalent nitrogen. Again wave mechanics does not offer any objections but is in full accord with these classical structures. While a decision between different sets of formulae and concepts cannot be reached by means of any of these additive molecular constants, spectroscopical evidence is leading farther and appears to favor the older classical system and its underlying concepts.

INTRODUCTION

THE first part of this paper[1] has shown an additive molecular constant, to wit the parachor, a function of the molecular volume, to be adaptable to two entirely different sets of chemical formulae. Additivity of the atomic or bond constants is achieved on either basis, although the concepts underlying the two sets of structures are entirely different. One of them works on the basis of different types of covalent linkage, directly or by virtue of resonance of different structures, while the other recognizes only one type of non-electrostatic bond. If no *raison d'être* was left for the classical structures, as often assumed, we are faced indeed with a situation as mysterious as it is logically unsatisfactory. At this juncture evidently a re-examination of the relation of both chemical theories with other additive molecular constants is called for. It will be seen that neither dipole moments (Section 3 of this paper) nor heats of formation (Section 5) nor bond distances (Section 4), etc., are able to distinguish between different theories or conceptions of the covalent linkage. In each case the grand total of a certain physical property of a molecule is measured, but the separation into atomic or bond constants is not an observed fact but an inferred deduction and therefore may be adjusted to any preconceived reasonable structure of the molecule. A simple physical reason can be suggested for this behavior (Section 6), but in any case it is obvious that such constants do not possess any diagnostic value as to different theories or types of the covalent bond.

Furthermore, the two chemical theories have to be compared with their wave mechanical equivalent (Sections 1 and 2). It will be seen (Section 6) that certain complications may be unified and simplified because the experimental basis on account of which they had been introduced does not stand up to a re-examining analysis and in fact does not exist. All this refers to molecules which belong to Werner's first order, and are formed by a definite central atom. They are energetically different from resonating aromatic or conjugate structures and the body of spectroscopical evidence appears to favor the classical formulae (Section 6).

In order to obtain a more clearly defined basis and terminology for the discussion of dipole moments, etc., most of the theoretical argument is taken up first and follows immediately (Sections 1 and 2).

1. WAVE MECHANICAL INTERPRETATIONS OF POLARITY AND OF DIFFERENT TYPES OF COVALENT BONDS

Different interpretations of the wave functions of a particular molecule are possible in wave mechanics; they are entirely compatible with

[1] R. Samuel, J. Chem. Phys. 12, 167 (1944).

each other and are in fact made use of by different schools of thought or by the same for different purposes. It might be as well to define clearly from the beginning which interpretation and hence which terminology is used in the following paragraphs.

Before doing so, however, another salient point of theoretical development might be recalled at the very outset, namely, that wave mechanics only knows one type of covalent linkage and does not recognize the concepts of the semipolar double bond or the singlet linkage. These concepts have been introduced into chemistry originally to save the so-called Octet rule (Lewis,* Langmuir, Lowry, Sidgwick, Sugden, *et al.*) and it is now often believed that wave mechanics has definitely established their existence in the form of resonance between covalent and electrovalent structures. However, a moment's reflection will show that this is not so. To be sure, resonance exists and, as the wave function of a molecule because of incomplete localization of the electrons between the nuclei, also contains a hybridization with ionic terms, the resulting linear combination may be interpreted as a resonance between covalent and electrovalent structures. But this is decidedly true of *all* covalent bonds, and only the contributions of the structures vary according to the ratio of the coefficients of their normalized functions. In this interpretation resonance with ionic parent structures does take place not only for molecules frequently described by means of a semipolar double bond, $-NO_2$, CO, $-NC$, etc., but for HCl, CH_4, H_2, and all others as well. The difference is not one of quality but of degree only, and sometimes not even that. We may call the bonds by whatever name we choose, but we are not entitled to differentiate between two groups and assume different kinds of linkage in them. Hence, the larger bond moment (to take this as an example of an additive molecular constant) of $N=O$ in the nitro group as compared with the nitroso stage may be ascribed to a larger ionic contribution, but not to a different type of linkage.

However, the description of the molecules as resonating between different structures, is only one of different but entirely equivalent interpretations.** As is well known, in an abbreviated form sufficient for our purpose the same wave function of the molecule AB may be written[2] either according to the view of the theory of molecular orbitals (of Herzberg, Hund, Lennard-Jones, and Mulliken) as

$$\Psi_{AB}=\{a\psi_A(1)+b\psi_B(1)\}\{a\psi_A(2)+b\psi_B(2)\},$$

and according to the requirements of the (Heitler-London, Slater, Pauling) electron pair bond theory of linkage the function is then written as

$$\Psi_{AB}=ab\{\psi_A(1)\psi_B(2)+\psi_B(1)\psi_A(2)\}+\{a^2\psi_A(1)\psi_A(2)+b^2\psi_B(1)\psi_B(2)\}.$$

Of these identical expressions, the second represents the molecule as resonating between the covalent structure $A:B$ and the ions B^+A^- and A^+B^- while the coefficients a and b determine the contributions of these structures. In the first the linkage is described as an ordinary covalent bond of a certain polarity. As the fields of the two nuclei, or rather of the two cores, are not identical, the field of the molecule possesses a certain dissymmetry, the analytical expression of which again is the ratio of the normalizing factors. This may be visualized as the electron pair being shifted slightly towards the negative partner, or belonging more to it in time, and if needs be it may be written, as has been done sometimes, as $A^{+\delta}-B^{-\delta}$, indicating a differential fractional charge. However, there is really no

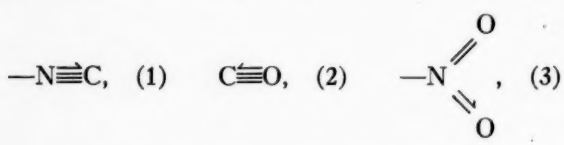
* However, Lewis himself always maintained the Doublet rule to be of vastly greater importance than the Octet rule.

** The possibility of different but entirely equivalent theories of valency is particularly clearly expressed by Pauling [L. Pauling, *The Nature of the Chemical Bond* (1938), p. 47]: "It is possible, on the other hand, to develop (at least in principle) a complete discussion of the structure of a molecule from either the purely ionic point of view (with extreme polarization or deformation of the ions), or the covalent point of view, provided that all the unstable atomic orbitals are used in the discussion. No treatment of either of these types has been carried out for molecules of any complexity, however, whereas the reasonable procedure which forms the basic of our argument has found extensive application to the problems of structural chemistry." The point of view adopted in this paper may be said to approach the second of the alternatives mentioned by him.

[2] Full details and references will be found in standard texts, e.g., in J. H. Van Vleck and A. Sherman's important summary in Rev. Mod. Phys. **7**, 167 (1935). Cf. also literature in H. Lessheim and R. Samuel, Proc. Ind. Acad. Sci. **1**, 623 (1935).

need for such a symbol. The formula cannot be supposed to indicate all properties of the molecule at a glance. Exactly as we do not indicate variations of bond energy by the different length of the printed line, we also refrain from indicating variations of polarity. The symbol $A-B$ therefore is understood to imply some polarity as long as the two atoms are not identical. The same physical fact, namely, the dissymmetry of the field, is described by both interpretations in a different way, and therefore each of the two wordings "covalent-ionic hybrid" or "polar covalent bond" explains or expresses not more and not less but exactly as much as the other. The ratio of the coefficient of the normalized functions also measures the degree of non-localization of the binding electrons. That is why the polarity of the molecule may be interpreted in these different ways. This also appears to be the underlying reason for the great difference of behavior between molecules formed by a marked central atom, under discussion here, and structures like the aromatic rings to which this paper does not apply. The latter are distinguished by non-localized electrons and rigorously identical energy values of the resonating structures; the former are best described by means of localized electrons and the energy differences between the resonating configurations are very large (cf. Section 6).

In this paper the first interpretation and terminology are made the basis of discussion. The reasons for this choice will become apparent below. At this stage attention may be drawn only to its greater simplicity. In Sidgwick's theory of coordinated bonds of simple inorganic structures the following molecules have to be written with a semipolar double bond thus:



$$-N\rightleftharpoons C, \quad (1) \qquad C\rightleftharpoons O, \quad (2) \qquad -N\begin{matrix}\overset{O}{\rightleftharpoons}\\ \underset{O}{\rightleftharpoons}\end{matrix}, \quad (3)$$

$$O=S\rightleftharpoons 0, \quad (4) \qquad O=Cl\rightleftharpoons 0. \quad (5)$$

If it is now attempted to embody as much as possible of these chemical concepts into a physical theory following the second interpretation, as has been done so carefully and ingeniously by Pauling,[3] the result is that the first of these structures is a hybrid between a covalent (electron pair bond) and only one ionic form, as expected. For the second, resonance of the covalent with two ionic forms obtains, which later cancel each other out, for (3) resonance of two ionic forms without any covalent structure, for (4) resonance between a covalent double and a covalent single bond, and for (5) a three-electron bond. To our mind there is nothing in the observable properties of the so-called coordinate bonds which calls for a separate and individual explanation of each or the introduction of a second variety of linkage.[3a] But if there should be, it is obvious that the interpretation on the basis of resonance with ionic structures does not yield a uniform theory, which would at least explain the additivity of molecular constants.

Another, and to our mind much more serious, discrepancy between both interpretations is the following: Both describe in different ways the same polarity of the molecule and therefore should arrive at identical expressions for the percentage of ionic contributions. But in many actual cases the results are widely different. In the above example for the orbital method the same ratio of the coefficients applies to both electrons in the same way, both the electrons being shifted towards the negative partner. Two electrons of 4.8×10^{-10} e.s.u. charge, shifted $0.1\text{A}=0.1\times10^{-8}$ cm will produce an electric moment of about 1×10^{-18} or 1 Debye unit. For gaseous HCl, the experimental moment of 1.28D therefore represents a shift of the bonding electron pair of 0.13A, which is about 10 percent of the internuclear distance of 1.28A. The orbital method therefore could be said to describe the molecule as 90 percent covalent and 10 percent ionic. From the pair bond view Pauling has made the same calculation, comparing the actual moment with that produced by the hydrogen electron, if transferred over the whole length of the internuclear distance, and obtains 17 percent

[3] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, 1938). (For details of structures, e.g., —NC, also literature mentioned therein.)

[3a] Physical properties are discussed in this paper and those referred to. An analysis of the chemical properties may be found in R. F. Hunter and R. Samuel, J. Chem. Soc., p. 1180 (1934); Chem. and Ind. **54**, 31, 467, 635 (1935).

ionic contribution. Such a calculation cannot be more than a rough estimate. Thus, the hydrogen electron could approach the Cl nucleus to its M shell only, while on the other hand the charge density distribution of the Cl^- ion still shows a considerable value at 1.28A distance from the nucleus, or, in other words, the radius of the Cl^- ion is larger than the bond distance of the HCl molecule. The estimate on the basis of the orbital method is not affected by such difficulties and therefore most probably more reliable, but under such conditions it is sufficient that both approximations lead to the same order of magnitude, indicating that both methods are in essential agreement as to the description of the observable facts in such an unambiguous case.

However, even the highest dipole moments recorded for polar covalent molecules fall into the order of 1.5 to 2D for a single and 3 to 4D for a double bond. For the latter, the shift of two pairs or 4 electronic charges has to be taken into consideration from the point of view of the orbital method. With the known internuclear distances, even the most favorable examples do not yield more than 10 to 15 percent ionic contributions according to the view of this theory, while 30 to 40 percent have been calculated for the description of the same molecules by means of resonating structures.

In some cases the uncertainty of experimental values will be responsible for this serious discrepancy, as is shown below (Section 5) for the carbonyl group. For another large class of molecules, formed by nitrogen, it is due to the fact that nitrogen is assumed to be not more than tetracovalent, and structures with pentacovalent nitrogen are excluded from consideration. The discussion of this assumption follows immediately (Section 2).

2. THE PENTACOVALENCY OF NITROGEN

If it were not for the purpose of establishing a clear terminology beforehand, the discussion of the pentacovalency of nitrogen would have been taken up at the end of this paper. The question is opened here not for the sake of an arbitrary supposition but because we are led to it by necessity. It will be seen below that all the physical constants of molecules formed by nitrogen, such as dipole moment, bond distance, and bond energy, behave similarly to the parachor, already dealt with in the preceding part of this paper. They can be represented as the sum of additive contributions of the constituent atoms on the basis of their classical formulae, if nitrogen is assumed to be pentacovalent. Again the pentacovalency of nitrogen is necessary to reconcile the findings of the pair bond theory and the molecular orbital theory as to the degree of polarity, as has already been indicated above. The results as to the additive molecular constants are sufficiently consistent not to take this situation as accidental, but to reconsider this question from its beginning.

Pentacovalency of nitrogen would originate from the excited electron configuration sp^4, similar to the sp^3 configuration of tetravalent carbon. As London[4] has shown, 2 of the p electrons would be chemically inactive, as they must be paired already in the atom on account of Pauli's exclusion principle, while d orbitals do not yet exist in this period. However, this is not so for polyatomic molecules where entirely different statements are derived from Pauli's principle on account of the axial symmetry of the field. It amounts to the simple fact that the possibilities for uncoupling the spin vectors of p electrons, originally paired in the atom, increase step by step from the atom to the diatomic, triatomic, polyatomic molecule. We may say that the l and λ properties of the electrons are successively lost in the formation of di- and polyatomic molecules. Another way of putting it is to count the number of free p orbitals, which increases step by step with the number of the constituent atoms, because the chemically active atoms always possess less p electrons than the following rare gas. However, just these points of view have been discussed earlier in detail[5] and a brief description of the formation of such a molecule by means of the orbital method will be sufficient here.

The combination of two unexcited N atoms in the configuration $(2s^2, 2p^3 - {}^4S)$ leads to the following configuration of the ground state of N_2:

$$\sigma^2(2s),\ \sigma^{*2}(2s),\ \pi^4(2p),\ \sigma^2(2p),$$
$$\{\pi^{*0}(2p),\ \sigma^{*0}(2p)\} - {}^1\Sigma.$$

[4] F. London, Zeits. f. Physik **46**, 455 (1928).
[5] H. Lessheim and R. Samuel, Phil. Mag. **25**, 664 (1938).

In the atom, each of the three p electrons occupies one of the two places in one of the orbitals $\lambda=+1, 0, -1$, as shown by the ^4S term. In the molecule, these electrons are shared in the corresponding $\pi(2p)$ and $\sigma(2p)$ orbitals which together represent the triple bond. But the free places of the atomic orbitals also have been "shared," and now form the premoted orbitals. These can be used again for the uncoupling of any pair. They have been added here, in parenthesis, marked by an asterisk for premotion and the superscript zero to indicate that they are unoccupied as long as N_2 is unexcited. If now an unexcited N atom combines with an excited one in the configuration $(2s, 2p^4, -^4P)$, i.e., posessing one s electron less and one p electron more, the following excited term of N_2 results:

$$\sigma^2(2s),\ \sigma^*(2s),\ \pi^4(2p),\ \sigma^2(2p),\ \pi^*(2p).$$

A singlet and a triplet Π term are formed, $^3\Pi$ being the lower one. The two unpaired electrons $\sigma(2s)$ and $\pi^*(2p)$ now may share their orbital with electrons of a third atom. One of them certainly is a premoted electron and we shall have to inquire presently whether it possesses bonding power, particularly in a polyatomic molecule. However, the first part of the argument is perfectly obvious: The two electrons which by necessity have been paired in the $2p^4$ configuration of the atom* have become uncoupled in the diatomic molecule. The excitation of the N_2 molecule by which this is brought about is in any case necessary, because unexcited N_2 and unexcited O could not combine to give the diamagnetic ground level of N_2O.

It may be mentioned that such a simple description would not be possible on the basis of the pair bond theory. Oxygen possesses the same $2p^4$ configuration of its p electrons in its unexcited state, and the above procedure essentially is nothing else but the building up of the ground state of O_2 from two unexcited atoms. The same process of uncoupling of electrons obtains for each of the two atoms and a configuration $[\ldots \pi^{*2}(2p)-^3\Sigma]$ results, which now contains two similarly unpaired electrons (one each being in π_+ and π_-). Indeed, the paramagnetism of the oxygen molecule is the direct experimental proof of this process of uncoupling of electrons previously paired in the separated atoms, exactly as the existence of the ozone molecule indicates the pentacovalency of nitrogen later on. The correct description of the oxygen molecule has been one of the early triumphs of the orbital method, but, as is well known, the pair bond theory could not obtain a paramagnetic O_2 molecule without resort to higher approximation. These may be gained[6] by considering the interaction of the normal with an excited term of the O atom, or of the corresponding electron configurations. Without too much inaccuracy these treatments may be described as making use of simultaneous but different distributions of the four p electrons over the three p orbitals. In this way, none of the three p orbitals is permanently taken up by a pair of electrons, but each of them alternatingly is occupied by a pair and by a single electron in the different distributions or terms. It appears evident that the same procedure applied to the excited sp^4 nitrogen atom instead of to s^2p^4 oxygen, will lead to a pentacovalent nitrogen atom, i.e., an excited N_2 molecule possessing two unpaired electrons.

Finally we have to investigate whether the unpaired but premoted electron of the excited N_2 molecule possesses bonding power. Here it should be recalled that all theories of valency in existence are only extrapolations of those few examples of molecules for which it has been possible to carry through the actual wave mechanical calculation. In order to be able to distinguish between established and assumed elements of these theories, we have to revert to the fundamentals on which they are based. Some of the points have already been discussed in greater detail elsewhere.[7]

Because the theories of valency cannot be established directly, but are generalizations only, however plausible, this process of extrapolation has to be guided and constantly corrected by experimental facts. Among them, of course, are such as known from band spectra, dipole moments, etc. But chemistry too has built up a

* As distinct from those of an s^2 group, which of course remain chemically inactive until the group is split by excitation.

[6] W. Heitler and G. Poeschl, Nature **133**, 833 (1934). G. Nordheim-Poeschl, Ann. d. Physik **26**, 258 (1936). G. W. Wheland, Trans. Faraday Soc. **33**, 1499 (1937).

[7] *a*. H. Lessheim and R. Samuel, Proc. Ind. Acad. Sci. **1**, 623 (1935). *b*. R. F. Hunter and R. Samuel, Nature **138**, 411 (1936); R. Samuel, Cur. Sci. **4**, 762 (1936).

large body of facts which also must play a leading role in the selection of those features of the simple molecules which should be extrapolated into a general theory of valency. In the chemistry of inorganic first-order molecules, numerical valency is a definite property of the free atom. It indicates its possibilities of reactions, although not all of them will lead to chemically stable molecules on energetical grounds. Characteristically, it is always in best agreement with the number and subdivision of the outside electrons of the atom. A theory of valency in which almost each molecular type needs special considerations to such an extent that the numerical valency of the atom occurs almost as a mere incident of the process of molecule formation—such a theory to the present writer at least appears to be less desirable than any other possible extrapolation in which the numerical valency of the free atom is one of the component assumptions by which the generalized theory is instituted.

While the electron pair bond theory essentially is a generalization from the point of view of the H_2 molecule, the orbital theory extrapolates the H_2^+ ion. To this fact is due the great importance as well as the great weakness of the latter. It permits the description of electronic configurations in terms of single electrons, but the bonding effect of the H_2^+ ion is due to the degeneracy of the two nuclear fields, and disappears the more the fields of the two atoms become unequal. It is therefore not the bonding effect which chemistry calls valency. Chemical covalency is produced by the degeneracy due to the identity of the electrons, which is always present, for equal and unequal atoms alike. Its prototype is the electron "resonance" of H_2 and because this effect is necessarily missing in the orbital theory, the latter is not a theory of valency at all, but essentially a description of the electron configuration of the completed molecule. As such it is greatly superior to the pair bond theory as the example of the O_2 molecule has shown. But because the electrons are treated essentially as independent, it leads (as is well known) to an entirely incorrect description of the process of formation (or, what is the same, of dissociation) of the molecule. Slater and Van Vleck* have demonstrated this in the example of H_2 and CH_4, which according to the orbital theory would be formed to 50 percent and to 73 percent, respectively, not from atoms but from ions. In order to convert the orbital method into a theory of valency, an additional assumption is necessary, and it is for this reason that the postulate has been introduced, according to which premoted electrons act antibonding. This can hardly be called even a generalization of H_2^+. Indeed, in the ground state of this molecule the electron is on a non-premoted orbital, but all the other terms of H_2^+ are unstable and not bonding* no matter whether the electron occupies a premoted or non-premoted group. To be sure, the premoted electron goes into an orbital of higher energy on decrease of the internuclear distance, and as in the united atom, it is bound with less energy to the molecule than the corresponding non-premoted electron. However, in a polyelectronic molecule, we do not know whether both the premoted and the corresponding non-premoted electron together are bound with more or less energy than in the correlated separated atoms. Or in other words, we do not know, whether compared with the corresponding non-premoted one, the premoted electron is bonding and contributes a smaller but positive amount to the energy of formation, or is antibonding, contributing a negative amount.

In most simple diatomic molecules only the lower premoted orbitals are occupied and a direct comparison with experimental evidence has not been possible so far. However, there is at least one excited term known, i.e., the $C^2\Sigma$ term of N_2^+, which appears to contradict this postulate.[8] In this term the molecule possesses an energy of dissociation which considerably exceeds that of the ground term. It is brought about by an excitation of the odd electron from the orbital $3s\sigma(2p)$ of the ground state to $3d\sigma(3s)$ of the excited level. Hence it furnishes an example of a non-premoted and therefore presumable bonding electron, whose excitation to an orbital of higher energy nevertheless strengthens the bond. This would appear not to be compatible with the basic

* Cf. reference 2.

* With one accidental exception at large internuclear distances.

[8] R. K. Asumdi and R. Samuel, Proc. Ind. Acad. Sci. **3**, 244 (1937). The term was found by W. W. Watson and G. P. Koontz, Phys. Rev. **46**, 32 (1934).

concept of the above postulate, according to which the change of energy of the system on the formation of the molecule is sufficiently described by the sum of such changes of the individual and independent electrons.

The introduction of the postulate of bonding and non-bonding electrons also does not fully permit the orbital theory to become a theory of valency, which represents the facts of covalent linkage as accumulated by chemistry. It clearly leads to the assumption, that all molecules with equal numbers of s and p electrons are bound by the same number of valencies. Thus BF possesses the same six p electrons on exactly the same orbitals as N_2 and the fact that either atom contributes three of them in the latter case, while one is supplied by B and five by F in the former is not taken into account. In order to do so, some special assumption has to be made, such as the higher nuclear charge of F keeping four of them on atomic orbitals. But then almost each molecule needs special considerations and explanations, and the simple system of inorganic chemistry is destroyed. Even so, the bonding effect of the degeneracy of the nuclear fields in H_2^+ makes the valency of an atom dependent on its partner not only in an energetic but also in a numerical sense, and the greater the difference of the nuclear fields the smaller must be the distance between them to bring about this bonding effect. This is certainly empirically not true, as a glance at the bond distances of the oxides of a period will show.

It is then simpler and clearer to follow an earlier suggestion of Hund,[7] to count as covalent bonds only those bonding pairs to which electrons are contributed by *different* atoms. In the frame work of the orbital theory this, of course, again is a postulate because this theory *per se* is unable to make any statement concerning the system of separated atoms, i.e., the completely dissociated molecule. But just for this reason some postulate is necessary if the orbital method shall be considered as a theory of valency, and this particular assumption does nothing less but to engraft into the orbital method the results of the pair bond theory, especially the electron "resonance" valency of Heitler and London. This way of counting immediately distinguishes the triple link of N_2 from the single link of BF, in spite of the identical electron configuration of both.* To the present writer this appears to be the procedure which is most economical in the number of assumptions, but permits the combination of results of the pair bond method at large internuclear distances with those of the orbital method at small ones, where it is supreme.

In such a procedure the energy of formation is due to the Heitler-London effect in the first instance, while premotion of electrons is a secondary effect by which it may be modified. It is of interest now to consider a pair of electrons, one from either atom, which together occupy a premoted orbital. If premotion was the only bonding effect, they should not constitute a link but act repulsively only. If it is a secondary effect, we may go one step further than Hund and expect a decreased bonding effect also in this case in which both the effects of electron degeneracy and of premotion counteract each other. Again only comparisons with experimental evidence can decide. Among the low terms of the light molecules only one is known suitable for this purpose, i.e., the double-excited term $2p\sigma_u{}^2-{}^1\Sigma_g$ of H_2. It is stable, the energy of formation being about 50 percent smaller than in the ground state $\sigma_g{}^2-{}^1\Sigma_g$. Here a pair of premoted electrons acts bonding, and (with the optimism recommended by Van Vleck and Sherman as a necessary ingredient of any theory of valency) the existence of this stable term might be generalized as well as that of the ground levels of H_2 or H_2^+. However, as the situation is complicated by the additional rigorous degeneracy of the nuclear fields, we confine ourselves to the statement that as far as diatomic molecules are concerned the identification of premoted with antibonding electrons is not a necessary part of the orbital theory, but has been introduced as an additional postulate. As that, it agrees neither with the well-established concepts of chemical valency nor with some of the experimental facts of band spectroscopy.

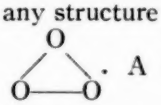
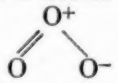
For polyatomic molecules the contention of pentacovalency of nitrogen becomes even more

[7] F. Hund, Zeits. f. Physik **73**, 1 (1931); **74**, 429 (1932).

* It should be noted that C in CO is divalent according to Hund's theory, in agreement with its parachor (Part I of this paper), its electric moment, bond distance, and bond energy (cf. Sections 4 to 6 below).

evident. As pointed out above, the kinematical nature of the quantum numbers of the electrons becomes less and less known, and with it the description and designation of the electrons at small internuclear distances less and less possible. It becomes less and less possible to predict whether the terms omitted in a simplified theory are not of importance, or else whether some of the higher roots of the secular equation classified as non-bonding are not actually such as to favor the binding of additional atoms. Hence two remarks may be sufficient to characterize the situation. First Mulliken's procedure[10] may be used to describe the electronic configuration from the point of view of a particular atom. In the above example of the excited N_2 molecule (containing one N atom excited to the pentacovalent state) the two unpaired electrons might be shared by a divalent atom, as in N_2O or in the similar case of $-NO_2$. Whether in such a molecule the electrons remain premoted ones from the viewpoint of the central N atom is difficult to decide; e.g., when replacing the two N atoms by the "united atom" Si, the two $3p$ electrons would be the shared ones of SiO, both being non-premoted. But without going into details, one point is clear, namely, that from the point of view of the O atom they form the fifth and sixth $2p$ electrons which are non-premoted. Furthermore, premotion, as well as being a statement about the energy by which the electron is bound to the nuclei, has also another physical meaning. The distribution of electric charge produced by the premoted electron between the nuclei is decreased when compared with that of the corresponding non-premoted one, the wave function of the former possessing at least one additional node between the nuclei. This is illustrated by the well-known Heitler-London diagram of the charge distribution of two repelling hydrogen atoms and may be considered as the origin of the postulate of the antibonding character of such electrons. But by virtue of the same argument, the charge distribution is particularly concentrated on the opposite side of the nuclei, and therefore in the polyatomic molecule such premoted electrons are particularly suited to be shared by additional atoms. Again this has been pointed out for certain cases by Mulliken in the same early paper.

The mechanism described here agrees with London's original paper[4] insofar as the higher valencies of atoms with three p electrons or more are not developed in the free and isolated atom itself. They can become active only in the stage of the triatomic molecule. Indeed the highest valency known in diatomic molecules and radicals is three; higher ones occur in polyatomic structures only. But once they have been developed, they are indistinguishable from the lower ones. The five bonds in N_2O are due to one s electron and four p electrons of the central N atom, hybridized similarly as in the case of tetravalent carbon. This view is entirely congruous with all the results of actual wave mechanical calculations. It differs from others only in the choice among the features presented for extrapolation by the simple molecules, one of which has to be generalized in order to span the gulf to the more complex ones. For all atoms maximal covalency immediately becomes identical with the number of their valence electrons in their outer shell, in agreement with the observed facts of chemistry.

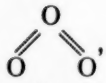
Finally, after these theoretical remarks, attention may be drawn to the ozone molecule. Once more, as for O_2, the electron configuration (s^2p^4) of the O atom makes tetracovalency of O the equivalent of the pentacovalency of N(sp^4). Recently Stand and Spurr[11] have shown that ozone forms an isosceles triangle with an angle of 122° at the apex. Together with the fact that a dipole moment of 0.5D has been observed[12] for it, this excludes any structure with equivalent O atoms such as  . A structure like  would possess a several times larger dipole moment.* But a structure with tretacovalent

[10] E.g., R. S. Mulliken, Phys. Rev. **40**, 55 (1932).

[11] W. Stand and R. A. Spurr, J. Am. Chem. Soc. **65**, 179 (1943).

[12] C. P. Smith and G. L. Lewis, J. Am. Chem. Soc. **61**, 3063 (1938).

* A resonance structure similar to that suggested by Pauling for SO_2, i.e., [O−O=O, O=O−O] might be possible, but there is no chemical indication that atoms of group VI act trivalent, and the paramagnetic term belonging to such a configuration should be the lowest one both for O_3 and SO_2. It is therefore difficult to accept it on the strength of the valence angle and bond distance alone. However, no low d orbitals exist for the O atom and by virtue of the same arguments by which N can be tetra-

oxygen at the apex, i.e.,  , is in best agreement with both (cf. Section 3). The structure of ozone may be considered as the direct experimental evidence for the pentacovalency of nitrogen. The premotion of the unpaired electrons of O_2 finds its expression in the decrease of the bond energy of the second double bond compared with the first one. (But already for SO_2, on account of the larger internuclear distance, this effect has almost vanished, as the atomic heat of formation of SO_2 is about twice that of SO.)

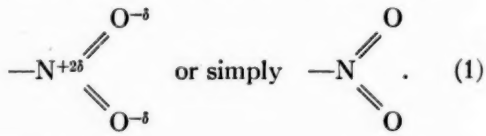
Summing up the argument, we may say that there is nothing in wave mechanical theories which prevents pentacovalency of nitrogen. The paired p electrons of its excited (sp^4) configuration become unpaired already in the diatomic molecule, as shown by the ground level of O_2. The antibonding character of its one premoted electron is the result of an additional assumption, the validity of which is highly doubtful already for diatomic molecules. For polyatomic molecules the bonding character of this electron (with respect to a third atom) appears to be evident even on the basis of this postulate. The ozone molecule seems directly to establish this contention.

Under these circumstances, approaching the empirical evidence without any preconceived view and taking it at its face value, it is difficult not to treat nitrogen as pentacovalent in such compounds as N_2O_5, exactly as on account of the divalency of oxygen boron is treated as trivalent in B_2O_3 or phosphorus pentavalent in P_2O_5, and chlorine heptavalent in Cl_2O_7. As B possesses 3, N and P 5, and Cl 7 valence electrons, this is indeed the much more consistent and satisfactory procedure. Nitrogen is pentacovalent only, it is true, if the atoms attached to it or at least most of them, belong to the second period, in combinations like $>C{=}N{\equiv}N$, $-N{=}N{\equiv}N$, $-O-NO_2$ (and may be NF_5 the existence of which has been reported).* But this is due to the great energy necessary for the transition from the s^2p^3 to the sp^4 configuration, the energy of fission of the s^2 group increasing from C towards F. This energy can be obtained only in conjunction with partners contributing the highest bond energies, and for the same reason oxygen never reaches the higher valence states of sulphur, and sulphur itself is hexavalent only in combination with O and F, but not with Cl or Br. These energetical conditions suggest themselves immediately as the true reason, if we compare the maximal valencies exhibited, e.g., by the atoms of the sulphur family against halides. They are:

OF_2	SF_6	SeF_6	TeF_6
OCl_2	SCl_4	$SeCl_4$	$TeCl_4$
...	...	$SeBr_4$	$TeBr_4$
...	...	...	TeI_4.

As the single-bond energy decreases from O to Te and from F to I, as well as the energy of fission of the s^2 group, it is apparent that only F provides sufficient energy to form hexavalent compounds of the heavier atoms. The other halides only come up to tetravalency, Cl from S onwards, Br only in combination with Se and Te, I with Te only. From Cl onwards they do not provide sufficient energy to obtain a positive energy balance for hexavalency and although the energy to be overcome includes the heats of sublimation and the dissociation energies of the diatomic molecules, most of it has to be ascribed to the fission of the s^2 group of the positive partner. No wonder that the even higher excitation energy of O is not overcome by any.

Accepting the pentacovalency of nitrogen, the structure, for instance, of the nitro group is

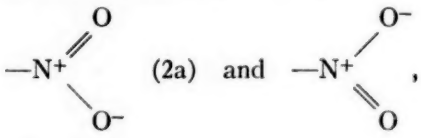


(1)

covalent only, the maximal covalency of O is two, and tricovalent as well as tetracovalent oxygen would establish the possibility of pentacovalency of nitrogen. For SO_2 and SO_3, G. E. Kimball [J. Chem. Phys. **8**, 188 (1940)] obtains structures and covalent double bonds, but with the help of d electrons, which in first approximation are not necessary in the present view and do not exist for oxygen as the central atom.

* L. Staub, Dissertation, Breslau, and private communication of Miss Staub. Along with nitrates of a number of metals, also ammonium nitrate has been found to be entirely covalent in the vapor state (below M.P.), and again for the ammonium nitrogen no other but a pentacovalent formula appears possible. [M. I. Haq and R. Samuel, Proc. Ind. Acad. Sci. **3**, 487 (1936).] NH_4Cl obtains one electrovalent bond by the intersection of the covalent with the ionic potential curve (as HCl or AgCl in solution), the additional energies of solvation, lattice, etc., being indispensable for this process. [Cf., e.g., R. F. Hunter and R. Samuel, Chem. and Ind. **55**, 733 (1936).]

The N=O bond is a simple covalent bond, i.e., two electron pairs, with a certain polarity superimposed according to the ratio of the coefficient of the normalized wave function; or in other words, according to the dissymmetry of the fields which itself is measured by the ionization potential and electron affinity of N and O. For the bond distance of structure (1) a theoretical value of 1.18A obtains (for the normal covalent double bond) according to Pauling's table,[3] in good agreement with the empirical value of 1.21 ± 0.02A. Its polarity may as well be termed resonance with the structures



(2a) and

, etc. (2b)

But these structures (2) are the only ones possible according to Sidgwick's theory and therefore the only ones recognized by Pauling. They form, however, much higher excited terms of the system. The level (sp^3) of N^+ needed for the ionic structure (2) lies 22.1 ev or about 500 kcal./mole above the term (sp^4) of N, required for the covalent structure (2), which amount is reduced to about 450 kcal./mole by the first electron affinity of O. The energy of formation of a semipolar bond N^+-O^+ may be estimated as the sum of the covalent N−O single bond of organic nitrates, plus an electrovalent bond such as LiF of the same period, or about 175 kcal./mole in all. Structure (2) therefore lies about 275 kcal./mole above structure (1) even without taking $D(N^5=O)$ into account. Hence the contributions of parent structures (2) are very small and the molecule is overwhelmingly represented by the classical structure (1). That is the inherent reason why the classical structures permit representation of the physical properties of the molecules, measured as additive molecular constants. This has already been seen for the parachor and will be shown also for the dipole moments and other similar constants. If nitrogen was not pentacovalent, all this indeed would hardly be understandable. At the same time it is evident how such a case of resonance differs entirely from the resonance, say, of the two Kekulé structures of benzene, in which latter case the two terms or electronic configurations indeed are associated with identical energy values. The resonance between covalent and ionic parent structures of inorganic molecules, which is the main subject of this paper, nowhere approaches this criterion. The two corresponding terms of the system are always separated by a considerable energy of excitation (often of the order of one or several bond energies). That is why the terminology of resonance is avoided here and instead that of the polar covalent bond (as defined in Section 1) is used throughout. According to the bond moment of 3.3D, the four binding electrons of each N=O bond of the nitro group are shifted from the center of electrical symmetry by 0.165A or 13 percent of the bond distance (1.21A) only. This may be taken as the order of the contribution of the parent structure (2).

3. DIPOLE MOMENTS AND BOND DISTANCES OF SOME TYPICAL MOLECULES

Dipole moments and the bond moments derived therefrom have been used in quite a number of attempts to establish the existence of the semipolar double bond and are assumed to establish large contributions of ionic structures justifying such formulae.[13] It is impossible to deal with all of them, as that would imply setting up in its entirety an alternative theory or system of bond moments. In such a theory *the change of valency* of the central atom would be responsible for any change of moment between the same atoms in different structures other than those due to a solvent or an induction effect of one moment on the other.* For outside reasons it appears impossible to work out such a system in all its details at this time, but a few examples will be sufficient to show such a theory to be entirely practicable.** Most of the typical structures whose electric moments have been discussed in connection with the coordinate linkage appear to involve the carbon and nitrogen atom

[13] For different opinions cf., e.g., the remarks on parachor and dipole moments of organic sulphur compounds in E. Bergmann, L. Engel, and S. Sandor, Zeits. f. physik. Chemie **B10**, 397 (1930).

* These two effects (of which only the former may be excluded in time by sufficient measurements in the gaseous phase) constitute inherent difficulties for any theory of bond moments and no greater or stricter additivity can be expected for one system, than for another.

** *Note added in proof:* A paper on bond moments and higher valence states is in preparation, which appears to lead to similar conclusions as have been obtained for the parachor in Part I.

and we shall confine ourselves to a discussion of the influence on the dipole moments exerted by a change of valency of these two atoms in a number of molecules.†

It may be seen from a comparison of the one radical the moment of which we know experimentally, i.e., nitric oxide, with the nitroso group, that this effect, which forms the basis of discussion here, really exists. The NO molecule differs from the $-N{=}O$ group by possessing a free odd p electron while for the latter the same electron is shared by another atom. The dipole moment of nitric oxide is 0.1D or less, the bond moment of the nitroso group is 2.0D. The transfer of a single electron of the N atom to an orbital on which it links another atom and is shared by it, reduces the negative charge on the positive end of the moment to such an extent that the latter is increased by 2 units.

The ozone molecule forms another typical example. From the discussion of the preceding section it has been seen that the dipole moment of 0.5D is too small for a semipolar double bond (or a resonance formula involving more than about 3 percent of an ionic parent structure), but its existence also rules out any formula based on three equivalent O atoms. The molecule therefore shows the existence of a moment between two oxygen atoms, one being in the divalent, the other in the tetravalent state. Because the ionization potential of oxygen is higher than that of sulphur, the dipole moment is quantitatively lower but otherwise similar to that of SO_2. Quite generally, namely, as long as bond angles, etc., remain unchanged, the bond moments should increase with the higher electron affinity of the negative and/or the lower ionization potential of the positive partner (e.g., $H-Cl=1.03>H-Br=0.78$, but $As-Cl=1.64<Sb-Cl=2.6$).

From the point of view of the orbital method, the existence of this type of moment always has been evident. The polarity of the bond can be obtained from the sum of ionization potential plus electron affinity of either atom, and the ionization potential of an atom obviously varies in different states of valency, in which different groups of electrons are involved. Indeed, the effect which is made the basis of discussion here is intimately related to the procedure successfully used by Mulliken[14] for the calculation of electroaffinities and for related problems. In the following it is attempted to find a qualitative understanding of the additivity of bond moments on the basis of classical structures.

As both the ionization potential and the electron affinity change in the same sense, in a homologous series a comparison of the former is sufficient to estimate the change of dissymmetry of the field and therefore the polarity of the bond. The mean ionization potentials again may conveniently be used, and a glance at the table in Part I of this paper shows, that the following moments will exist (here and later the superscripts designate different states of covalency, not ionic charges!):

$$N^5{\rightarrow}N^3>N^3{-}N^3,\quad N^5{\rightarrow}O>N^3{\rightarrow}O,$$
$$N^5{\rightarrow}C^4>N^3{\leftarrow}C^4,\quad N^3{\leftarrow}C^4<N^3{\rightarrow}C^2,$$
$$C^4{\rightarrow}O>C^2{\rightarrow}O,\quad O^4{\rightarrow}O^2>O^2{-}O^2.$$

This method of estimating the polarity of the bond by means of the dissymmetry of the axial field has the advantage of being based on directly observed quantities.

Nitrous oxide will serve as a typical starting point. Its electric moment is low, $\mu=0.1$ to 0.2D. As the moment of N_2 is of course zero, while the NO structure shows quite a large moment in the nitroso group ($\mu=1.65$ to 2.0D) the small moment of N_2O was thought to require special explanations. Thus Sutton[15] gives the two formulae (3a) and (3b).

$$N{\leftrightharpoons}N{=}O \quad \text{or} \quad :\dot{\underset{\cdot\cdot}{N}}::N::\dot{\underset{\cdot\cdot}{O}}:, \qquad (3a)$$

$$N{\equiv}N{\rightleftharpoons}O \quad \text{or} \quad :N:::N:\dot{\underset{\cdot\cdot}{O}}:. \qquad (3b)$$

Pauling[3] accepts these two structures, but writes them closer to Lowry's concept of the semipolar double bond thus:

$$:\underset{\cdot\cdot}{N}{=}N{=}\underset{\cdot\cdot}{O}:, \quad (4a) \qquad :N{\equiv}\underset{\cdot\cdot}{N}{-}\underset{\cdot\cdot}{O}:; \quad (4b)$$

† All dipole moments of molecules mentioned without reference are taken from the compilations in Trans. Faraday Soc. **30** (1934). All bond moments for which no reference is given refer to those calculated by C. P. Smyth [J. Am. Chem. Soc. **60**, 183 (1938) and earlier] which have been used as the basis of the following calculations. Internuclear distances are taken from L. O. Brockway, Rev. Mod. Phys. **8**, 231 (1936), if not mentioned otherwise.

[14] R. S. Mulliken, J. Chem. Phys. **3**, 573 (1935).
[15] L. E. Sutton, Trans. Faraday Soc. **30**, 789 (1943).

showing more clearly that the semipolar double bond involves the complete transfer of an electron from one atom to another. On the basis of known or plausible internuclear distances the bond moment of these forms may be computed. For N_2O only the sum of both distances has been measured to 2.38 ± 0.05A by electron diffraction and 2.31A from spectroscopic data.[16] However, this is sufficiently near to the sum of Pauling's covalent radii, *viz.*, 1.10 for N≡N and 1.18 for N=O. Using such values Sutton is able to calculate the moments of the two structures thus:

$$:\overset{\ominus}{\underset{\cdot\cdot}{N}}=\overset{\oplus}{\underset{\cdot\cdot}{N}}=\underset{\cdot\cdot}{O}: \quad (4a) \qquad \text{and} \qquad :N\equiv\overset{\oplus}{N}-\underset{\cdot\cdot}{\overset{\cdot\cdot\ominus}{O}}: \quad (4b)$$

$$\overset{\leftarrow\!+}{\mu=5.3}-\overset{+\!\rightarrow}{1.65}=3.65 \qquad \mu=0-5.8-\overset{+\!\rightarrow+\!\rightarrow}{0.8}=-6.6.*$$

It is now assumed that resonance exists between the two structures, (a) contributing so much more that the small moment of about $\mu = 0.1$ is observed. Agreement with experimental facts of course can always be achieved this way.

In the alternate theory nitrous oxide possess the simple structure N≡N=O, or, as electronic formula

$$:N:::N::\underset{\cdot\cdot}{O}: \qquad (5)$$

in which the triple and double bond consists of 3 and 2 pairs of electrons, half being contributed by either atom. However, comparing N_2

$$:N:::N: \qquad (6)$$

with (6) it is immediately evident that an electric moment is produced by the change of the valence state of N. In the transition from N_2 to N_2O, the central N atom partially loses two electrons now shared with O; it becomes a center of positive polarity and the $N^3 \equiv N^5$ group is no longer symmetrical but will possess an electric moment of considerable strength. At the same time and for the same reason the moment of the N^5=O group must be much larger than that of the N^3=O group, the positive character of N being enhanced by the partial removal of two electrons. Taking the experimental results at their face value, the dipole moment of nitrous oxide can be used to determine the moment of the $N^3 \equiv N^5$ group. The N^5 atom being the positive center, the small moment of N_2O is but the very natural result of two opposing moments. The N^5=O moment cannot be that of the nitroso group in which N is trivalent. The nitro group exhibits about the same internuclear distance (1.21A) as N=O in N_2O, and its moment of 3.3D will be that of the N^5=O bond. It is larger than the N^3=O moment of the nitroso group quite in keeping with the view developed here.

The moment of N_2O may now be described thus:

$$N^3 \equiv N^5 = 0$$
$$\overset{\leftarrow\!+}{\mu=-3.1}+\overset{+\!\rightarrow}{3.3}=0.2,$$

and there remains only to show that this is not an assumption *ad hoc*, but that a similar moment of $\mu = 3.1$ is associated with the group $N^5 \equiv N^3$ in other molecules too.

Attention may therefore be drawn to the organic azides and diazo compounds both frequently quoted as standard examples of molecules containing the semipolar double bond or resonating between corresponding ionic parent structures. The older structural formula R—N= N≡N has already been found entirely sufficient to calculate the molecular parachor (Part I of this paper). It will be seen that this formula and the related one R_2=C=N≡N for the diazo compounds are entirely sufficient to describe their dipole moments and also the internuclear distances.

For this purpose, however, it is necessary first to evaluate the bond moments of the groups N^5=N^3 and N^5=C. It should be possible to calculate these directly from the known moments of normal and iso-azoxybenzene, and of the N ethers of the benzaldoximes, used by Sutton and Taylor[17] to determine the isomeric forms. But the uncertainty as to valence angles prevents such a calculation without further experimental data.* Fortunately rough values of bond mo-

[16] E. K. Plyler and E. F. Barker, Phys. Rev. **38**, 1827 (1931).

* The moments 5.3×10^{-18} and 5.8×10^{-18} are the charge of the electron, 4.8×10^{-10} multiplied with the distances 1.1×10^{-8} and 1.2×10^{-8}, respectively, $\mu = 1.65$ is the moment of the nitroso group R−N=O, $\mu = 0.8$ half of it, the double bond being replaced by a single bond.

[17] L. E. Sutton and T. W. J. Taylor, J. Chem. Soc., p. 2190 (1931); p. 63 (1933).

* Substituting a few extreme values of the valence angle, it can be seen that the $N^5 = N^3$ moment probably will be between 1.5 and 2.0D, directed against N^3, the $C^4 = N^5$ moment between 1.0 and 1.5D pointing against C, both directions in agreement with the present view.

ments, as so often in the past, can be obtained by a number of different extrapolations. For the $N^5{=}N^3$ moment a rough value would be two thirds of the $N^5{\equiv}N^3$ moment, or 2.0D. But as the polarity depends on the ionization potentials and electron affinity, a better way is offered by the great similarity of the positive atoms C^4 and N^5 and the negative atoms O^2 and N^3. As $\mu(C^4{=}O)$ is higher than $\mu(C^4{=}N^3)$ by $2.5-0.9=1.6$, and as the same factors are working in both cases, $\mu(N^5{=}O)$ should be about as much higher than $\mu(N^5{=}N^3)$ and the latter therefore about 1.7D, particularly as the internuclear distance of both are almost identical. The moment of $N^5{=}C$ cannot be obtained this way, because the mean ionization potential indicates a change of sign, if compared with $N^3{=}C$. Hence, falling back to the first procedure, we calculate $\mu(N^5{=}C)$ by adding two thirds of 3.1 for the valence change to $\mu(N^3{=}C)$, $-0.9+2.0=1.1$, and adding an allowance for the increase of bond distance as compared with $N{\equiv}N$, we choose 1.5D as a rough final value.

The dipole moments of the azides, to which we now may turn, have been determined by Sidgwick, Sutton, and Thomas[18] to between 1.4 and 1.6D pointing away from the organic radical. Sidgwick[19] and Pauling[3] again assume resonance between two structures, which may be written in different ways as follows:

$$R{-}N{=}N{\rightleftharpoons}N, \quad \text{or} \quad R{-}\ddot{N}{=}\overset{\oplus}{N}{=}\overset{\ominus}{\ddot{N}}:,$$

$$\text{or} \quad R:\ddot{N}::N::\ddot{N}: \qquad (7a)$$

$$R{-}N{\leftharpoons}N{\equiv}N, \quad \text{or} \quad R{-}\ddot{\overset{\ominus}{N}}\,{-}\overset{\oplus}{N}{\equiv}N:,$$

$$\text{or} \quad R:\ddot{N}:N:::N:. \qquad (7b)$$

As for N_2O, opposing moments of the order of $\mu=4$ are estimated, both contributing to the empirical value. In the present view the azides have to be represented by the formula:

$$R{-}N^3{=}N^5{\equiv}N^3 \qquad (8)$$

and their moment by

$$\begin{matrix} -N^3{=}N^5{\equiv}N^3 \\ \leftrightarrow\!+\!\rightarrow \end{matrix}$$

$$\mu=-1.7+3.1=1.4; \quad \mu_{obs}=1.4 \text{ to } 1.6.$$

A better agreement cannot be expected. The internuclear distances have been measured by electron diffraction and agree perfectly well with those calculated on the basis of the formula (8) thus:

	$H_3C{-}N{=}N{\equiv}N$			
r [observed]:	1.47	1.24	1.10	$\pm$0.02A.
r [calc. for (8)]	1.47	1.22	1.10.	

Bond distance, bond moments, and parachor agree exceedingly well with formula (8). Any other one being a highly excited term of the molecule, it seems to be overwhelmingly represented by this classical structure.

The aromatic diazo compounds R_2CN_2 suggest themselves as a further instance to check the present procedure. Their dipole moments have been determined by Sidgwick, Sutton, and Thomas[18] ($\mu=1.4$) and their formula has been discussed by Sidgwick[19] at various occasions on the basis of coordinate or resonating structures, similar to those of the azides. Without repeating the previous argument their structure and moments may be represented immediately by the classical formula thus:

$$\begin{matrix} R \\ \diagdown \\ C{=}N^5{\equiv}N^3 \\ \diagup \\ R \end{matrix} \qquad (9)$$

$$\mu=-1.5+3.1=1.6; \quad \mu_{obs}=1.4.$$

A better agreement could not be expected. As to the bond distances, a linear structure with $r(CN)=1.34\pm0.05$A and $r(NN)=1.13\pm0.04$A has been observed, against 1.28 and 1.10A, respectively, calculated for structure (9). Again it is obvious that this classical formula agrees perfectly well with both molecular constants and there is no need to amend it in any way.

At the same time it is shown that the moment of 3.1D, produced by the change in the state of valency, is constant and definitely associated with the $N^5{\equiv}N^3$ structure both for the azides and diazo derivatives.

The second group of molecules most often said

[18] N. V. Sidgwick, L. E. Sutton, and W. Thomas, J. Chem. Soc., p. 406 (1933).
[19] N. V. Sidgwick, Trans. Faraday Soc. **30**, 801 (1934); Chem. Rev. **19**, 183 (1936).

to establish the existence of a semipolar double bond or the fact of enhanced resonance in simple inorganic molecules is that formed by divalent carbon. In the same way the change of bond moments produced by the change of valency of this atom may be used to throw light upon their structure.

The bond moment of carbon monoxide is small, $\mu = 0.1$, that of the carbonyl group large, $\mu = 2.5$. Hence for the former the formula

$$C \equiv O \quad \text{or} \quad :\overset{\ominus}{C} \equiv \overset{\oplus}{O}: \quad \text{or} \quad :C:::O: \qquad (10)$$

has been suggested.[20] Pauling[3] assumes resonance between this structure, the ordinary structure $C^2{=}O$, and a third one in which C is a positive and O a negative ion, linked by a single bond, thus

$$:\overset{\oplus}{C}:\overset{\ominus}{\underset{\cdot\cdot}{O}}: \quad (11a) \quad \text{plus} \quad :C::\ddot{O}: \quad (11b)$$

$$\text{plus} \quad :\overset{\ominus}{C}:::\overset{\oplus}{O}:. \qquad (11c)$$

One of the reasons for introducing the third structure (11a) is the good agreement between the observed internuclear distance of 1.13A with the sum of the covalent radii for the old formula (11b), which is 1.15A. This indicates structure (11b) as the only one present; any resonance of C=O (11b) with C≡O (11c) makes the straightforward empirical result not understandable. Therefore, a third structure (11a) has to be assumed in such a way that (11a) and (11c) cancel each other out entirely [both together representing a molecule with $\frac{1}{2}(1+3)=2$ normal covalent bonds and no charges on either atom]. All three together in reality amount only to the classical formula (11b). This structure, to our mind, is in entire agreement with the electron configuration of C (s^2p^2), only the p electrons being active, as in N^3, etc., and the chemical and physical properties of the molecule. If therefore it could be shown that the dipole moment does not force resonance upon the carbon monoxide molecule, nothing would prevent the acceptance of the old formula $C^2{=}O$.

This can in fact be done, the only difficulty being the small number of compounds formed by divalent carbon. The best way therefore appears to calculate the effect of the change of valency from C^4 to C^2 as indicated by CO, and then to see whether a similar value again occurs in the isocyanides $R{-}N{=}C^2$.

Again taken as they are found, and without any theoretical assumption as to a change of linkage, the empirical results of dipole measurements lead to the following simple structures for the CO group in carbon monoxide (12) and in the carbonyl radical (13):

$$:C::\ddot{O}: \quad (12) \qquad \text{and} \qquad \begin{matrix} & & R \\ & & \cdot\cdot \\ & & C::\ddot{O}: \\ & & \cdot\cdot \\ & & R \end{matrix} \quad (13)$$

$\mu = 0.1$ (12) $\qquad$ $\mu = 2.5$. (13)

In the first, the C atom forms the positive end of the moment, but only its p electrons are chemically active, the two remaining electrons of its symmetrical s^2 group still screen the nuclear charge. The four bonding electrons are in the field of O^{6+}, screened by 4, and C^{4+} screened by 2 electrons, the dissymetry of the axial field is therefore slight. In the other structure, the two s electrons (one having been excited) now are chemically active, i.e., occupy molecular instead of atomic orbitals. They belong partially to the organic radicals; their screening effect has diminished almost to the vanishing point. This amounts to a large positive charge having been added to the positive end of the C=O dipole. No special theoretical concept is necessary to understand fully the difference of moment. Therefore, it may be stated, that this difference most certainly does not provide evidence for the existence of resonance of the CO molecule with ionic parent structures, in which more than 2 of the p electrons of oxygen take part in the linkage.

From this it would appear that the valence change of C produces an increase of the C=O moment of 2.4D. While the moment calculated for the $N^5{\equiv}N^3$ group in one molecule could be shown to exist also in others, such a simple procedure is not possible in the case of $C^2{=}O$, the carbon atom being divalent only in the combinations C=O and C=N—. This new value therefore has to be compared with the bond

[20] D. L. Hammick, R. G. A. New, N. V. Sidgwick, and L. E. Sutton, J. Chem. Soc., p. 1876 (1930). Cf. references 15 and 19.

moment of the iso-cyanides. Although the molecule CO and the radical C≡N— are quite similar in some respects, they are not identical. In particular, the internuclear distance is 1.13A in CO and 1.17A in CN—, and the moment as the product of both, charge and distance, is as sensitive to the one as to the other. Two pairs of electrons shifted a distance of 0.04A would produce an addition to the moment of 0.8D. Added to the above value, 3.2D obtains, and the moment of $—N^3{\equiv}C^2$ in the isocyanides should be smaller by this amount than that of $—N^3{\equiv}C^4{=}$ of the isocyanates.

The isocyanides form straight chains,* and their dipole moments have been measured by Hammick, New, Sidgwick, and Sutton,[20] together with their parachors, which have been discussed in Part I of this paper. Their measurements on substituted benzenes show clearly that the NC bond moment points toward C and for the moment of the isocyanide group a value of 2.3*D* is obtained. They formulate the group as

$$—N{\equiv}C \quad \text{or} \quad —\overset{\oplus}{N} : : : \overset{\ominus}{C} : \qquad (14)$$

and consider the moment as that of the cyanide group superimposed on a second one of opposite sign produced by the transfer of an electron along the whole internuclear distance. Pauling believes the radical to resonate between this structure (14) and the older Nef formula

$$—N{=}C^2 \quad \text{or} \quad —\ddot{N} : : \ddot{C}. \qquad (15)$$

Incidentally, the internuclear distance is observed to 1.17± 0.02A; the sum of Pauling's covalent radii (with the usual allowance for the incomplete valence shell of C) comes to 1.19. Hence even on this basis and taking the internuclear distance as the main indicator, no resonance with (14) is required and the sole use of the Nef formula is entirely justified.

On the basis of the formula $—N^3{=}C^2$, the bond moment may be compared with that of $—N^3{=}C^4$, thus:

$$\underset{\mu=0.9}{O : : C : : \overset{\cdot\cdot}{N}—R} \qquad \underset{\mu=0.9-3.2=-2.3;\ \mu_{obs}=-2.3.}{\overset{\cdot\cdot}{C} : : \overset{\cdot\cdot}{N}—}$$

In other words, the return of two previously shared electrons into the s^2 group of the C atom, when becoming divalent, screens the field of the C^4 nucleus and adds additional negative charge to the C— end of the moment. Using for the latter the figure calculated from carbon monoxide, a moment obtains which has the correct numerical value and the right direction. Although this is a very simple and straightforward interpretation, the scarcity of molecules formed by divalent carbon with which to compare molecular constants makes a further and a more conclusive analysis impossible.

The numerical values used here certainly are very rough, and the preceding calculations do not pretend to be more than a short preview of a future detailed calculation. But even so these few examples are sufficient to show a separation of dipole moments into bond moments according to the state of valency of the positive atom to be entirely practicable and workable. This may be said with even greater confidence as the molecules chosen here are just those often considered as standard examples for the existence of additional varieties of covalent bonds.

The fundamental difference of the two representations may be demonstrated by considering again the linkage of the simple molecule CO. The observed fact is that the moment is smaller than that of the carbonyl group. According to Sidgwick it is a triple bond, the third link produced by 2 additional electrons of oxygen. In Pauling's terminology this bond is represented by resonance with a structure in which C is a negative, O a positive ion. In the present representation the greater negativity of C as compared with the carbonyl carbon is produced by its own s^2 electrons. Therefore only two and not four electrons of the oxygen take part in the linkage at any time. The bond is an ordinary covalent double bond. The polarity of this bond is very slight because the fields of the two nuclei are very similar as long as C is divalent. This may be represented by an exceedingly slight resonance of the Nef structure (12) with Pauling's structure (11a), but not with (11c). The almost vanishing smallness of the ionic contribution is again indicated by the bond distance calculated for the Nef structure, being almost identical with the observed one. This representation is not only

* As carbon is divalent, they are entirely different from the oximes and no conclusion as to the type of linkage could be based on a comparison of the valence angles of both.

in accordance with all observed facts, straightforward and simple, but it also has the additional advantage that oxygen in linkage with carbon has not suddenly become the positive partner, entirely contrary to its electron affinity and to the observable and known ionization potentials of both.

It is beyond the scope of this paper to extend this procedure to other molecules, determining, for example, the different values of the S=O bond moment according to the valence state of S. The differences will be less marked, as can be seen from the ionization potentials, but a similar set of values could be derived. However, attention should be drawn in passing to the new evidence brought forward recently by Sutton *et al.*, indicating very definitely that such bonds are ordinary covalent double bonds.[21] Bond distances of 1.4, 1.5, and 1.9A having been observed[22] for S=O, P=O, and P=S, respectively, it has been computed that their moments should be 6.9 to 9.3D if they are semipolar double bonds, i.e., structures with large ionic contributions. The experimental bond moments are only 2.16, 3.5, and 2.5D in solution[23] and 2.0 to 2.5, 3.5, and 2.5D, respectively, in the gaseous state.[24] Conditions are similar for N=O in trimethylamine oxide.[25] Although these calculations of the bond moments neglect by necessity the ordinary induction effect and also that of the change of valency, the order of magnitude must be correct, and no such objection can be raised against the low value of the S=O moment in SO_2. The dipole moment therefore again decides against the coordinate linkage or enhanced resonance with ionic structures in such molecules as SO_2, $SOCl_2$, $POCl_3$, etc., which have been taken as its prototype for such a long time.

Polarity and resonance are made use of in modern physico-chemical theories for the rationalization of such concepts as acid strength or reactivity. It is not likely that excessive changes would be brought about in these theories by the present interpretation. The electric moments are observed facts and the results of their working cannot be affected by the causes to which we attribute their existence. We may obtain a different theoretical model but similar results of actual calculation. Thus, the ionic contributions (viewed either as resonance with ionic parent structures or as an electric strain of the covalent bond) in the present view is much reduced for a great class of molecules, e.g., for the nitro group from 100 percent to 13 percent. In theories of acid strength, to take these as an example, the "resonance" factor would almost vanish but the new effect of valence change will take its place. The effective field of the central atom will increase its strength in the higher valencies compared with the lower ones, where it is screened by its two *s* electrons. A general shift of the electrons in the direction of the central atom results. This may be added to the inductive effect, and different inductive factors for the same atom in different states of valency will take the place of the resonance factor. Such a model automatically should work just as well as the description by means of resonance because both are equivalent interpretations of the same fundamental wave mechanical concepts.

4. BOND DISTANCES

The bond distances again belong to the class of additive constants of the molecules which is discussed here. The distance between the nuclei, it is true, is directly observed, but any conclusion as to the chemical structure of the molecule is based on the separation of the bond distance into contributions of the constituent atoms.[26] Although conditions are slightly different for the bond distances than for other constants, it happens that one constant per atom is not sufficient to represent the experimental values and therefore different subdivisions according to various theoretical viewpoints are again pos-

[21] L. E. Sutton, Ann. Repts. **37**, 74 ff. (1940), London, 1941.

[22] Cf. literature in reference 21.

[23] C. P. Smyth, J. Am. Chem. Soc. **60**, 183 (1938); C. P. Smyth, G. L. Lewis, A. J. Grossman, and F. B. Jennings, *ibid.* **62**, 1219 (1940).

[24] I. E. Coop and L. E. Sutton, Trans. Faraday Soc. **35**, 505 (1939).

[25] Cf. reference 21. As compared with the nitro group, the bond distance is increased from 1.21 to 1.36A. Hence the increase of the moment from 3.3 to 4.38D does not call for a special explanation by means of an enhanced contribution of an ionic structure. This moment represents a shift of two pairs by about 16 percent of the bond distance.

[26] Values of a covalent radii are taken from Pauling, reference 3. Cf. also V. Schomaker and D. P. Stevenson, J. Am. Chem. Soc. **63**, 37 (1941) for influence of polarity.

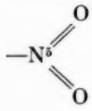
sible. Besides the different values of the additive covalent radii for multiple bonds, a number of factors have been made responsible for the deviations between the observed and calculated values, among them the variations of polarity or of the contributions of different structures, an incomplete valence shell (which amounts, e.g., for C to different radii for different valence states), and different quantum numbers of the binding electrons. The change of valence state, of course, has often been considered as a decisive factor, and might be called upon to solve a number of difficulties if considered *in conjunction* with a polarity factor and with the different role of an atom as the positive or negative partner in a molecule.

The discussion of this particular property of the molecules is made more difficult at this time because the experimental evidence is still rapidly changing. New evidence brought forward recently[21] has shown the whole question to be more complex than originally thought. Very roughly the present situation may be described as follows: Among organic molecules the observed bond distances agree with the theoretical ones with the exception of some molecules of enhanced polarity [cf. fluorides or the differences of the $N^5{=}O$ distance in the nitro group (1.21A) and amine oxide (1.36A)].

Among the organic molecules some indication of an influence of different states of valency is apparent, e.g., Pauling's reduction of 0.09 for C in CO as allowance for incomplete valence shell. If, however, the experimental CO distance in the carbonyl group is compared directly with that in carbon monoxide without regard to the theoretical value, it is found that it sometimes has the same value (CO_2, CH_2O, CH_3COCl) and sometimes the higher theoretical value ($COCl_2$, CH_3CHO).

Among inorganic molecules, i.e., taking into consideration a greater number of different atoms, the bond distance is found to be remarkably insensitive to a change of valence. For instance, the SO distance is identical in SO_2, $SOCl_2$, SO_3, SO_2Cl_2, and even agrees not too badly with the spectroscopical value of SO. On the other hand the bond distances do not agree well with the theoretical values any longer, some being too large and most of them too small. The discussion has not reached a definite conclusion; serious objections have been raised against various suggested explanations. It appears to be evident, however, that the polarity of the bond is one of the determining factors, although perhaps not the only one. Another simply might be that the additive covalent radius say of S, obtained from S_8 molecules, works satisfactorily only in simple organic molecules in which this atom almost invariably is the divalent negative partner, but not in SO_2, where it forms the positive end of the dipole and is tetravalent. An introduction of a polarity factor, while improving some of the older agreements, impairs others. But this may be recorrected by a constant for valence change.

TABLE I.

Molecule	Bond	Bond distance observed	Bond distance calculated for the classical structure of column 1
	$N^5{=}O$	1.21±0.02	1.18
$N^3{\equiv}N^5{=}O$	NN+NO	2.31 to 2.38	2.28
$-N^3{=}N^5{\equiv}N^3$	$-N^3{=}N^5$ $N^5{\equiv}N^3$	1.24±0.02 1.10±0.02	1.22 1.10
$>C{=}N^5{\equiv}N^3$	$C{=}N^5$ $N^5{\equiv}N^3$	1.34±0.05 1.13±0.04	1.28 1.10
$C^2{=}O$		1.13	1.15
$-N^3{=}C^2$		1.17±0.02	1.19

In this rather complicated situation it is not easy to appeal to the bond distance for definite guidance as to the structure of a molecule for which different concepts are possible. We confine ourselves therefore to the statement that in all those standard examples which we have considered (Section 3), i.e., the molecules $-NO_2$, $N{\equiv}N{=}O$, $-N{=}N{\equiv}N$, $>C{=}N{\equiv}N$, $C{=}O$, and $-N{=}C$, the bond distances are in excellent agreement with these classical structures. They are summarized in Table I (in which the superscripts again mark the state of valency, not electric charges).

In the case of resonance of two structures, of which the first has a higher and the other a lower theoretical value if compared with the experi-

mental one, agreement can always be achieved by assuming an appropriate percentage contribution of each form. This is not possible if only one classical formula serves as the basis of calculation and this surprising agreement is therefore even more convincing. It appears therefore extremely difficult to avoid the conclusion that no objections can be raised on the grounds of bond distance against an interpretation which considers the classical structures (including those of pentacovalent nitrogen) as the nearest approach to reality.

5. BOND ENERGIES

Finally, the bond energies have to be discussed. However, only a few words are necessary here. The experimental facts are similar to those observed for other molecular constants. If from the heat of formation the heat of dissociation D of the gaseous molecule into gaseous atoms is calculated,[27] e.g., for PCl_3 a value of 343 kcal./mole obtains, i.e., an average bond energy D_B of the P−Cl bond of 87. The same procedure gives the smaller value of $D_B=69$ for the P−Cl bond in PCl_5. One way to account for this difference is to assume two of the chlorine atoms to be linked to phosphorus differently as compared with the others. However, the other alternative is to consider the valence change of the central atom. While the Cl atoms in PCl_3 are linked by the three p electrons, for the transition to PCl_5 the two inert s electrons have to be activated. The fission of the s^2 group, i.e., an excitation of the PCl_3 molecule, absorbs energy to such a considerable extent that the ground level of PCl_5 lies much closer to that of PCl_3 as it would do if PCl_5 were formed by a combination of unexcited PCl_3 and two unexcited Cl atoms. This has been discussed at length in connection with the dissociation spectra of a great number of inorganic and organic molecules;[27,28] a general rule applicable for every spectrum investigated so far, could be formulated, and in the case of SO, SO_2, and SO_3 where most spectroscopical data are available, an energetical interpretation of what is called the semipolar double bond could be given.[29] According to this interpretation the true bond energy of S=O in SO_3 is not diminished, but the energy of the reaction SO_2+O does not measure it, because the ground level of SO_2 is not the term from which that of SO_3 originates. To our mind this interpretation is definitely established, because this energetical relation of the ground levels of SO_2 and SO_3 is independently confirmed. If, for instance, unexcited (diamagnetic) SO_2 and unexcited (paramagnetic) O would combine to give the ground level of SO_3, this would be a paramagnetic molecule. But as is well known, all the molecules to which this reasoning applies, i.e., PCl_5, $POCl_3$, $PSCl_3$, SO_3, $SOCl_2$, Cl_2O_7, etc., are diamagnetic.

The bond energies therefore constitute a molecular constant which again could be divided into additive increments in different ways and in accordance with either of two discordant chemical theories, only that in this case the one favoring the coordinate bond of such molecules appears to be ruled out by conflict with the experimental spectroscopical and magnetic evidence.

A short discussion of Pauling's procedure to calculate directly the contributions of the ionic structures to the energies of the various bonds may be inserted at this point. It has been pointed out above (Section 1) that such estimates according to different theories do not agree for a number of typical molecules. It can be seen that this is due to certain basic energy values. Their determination in our view has not reached a point where conclusive deductions could be reached for these controversial structures.

First of all, Pauling's system of electronegativities is based on a set of single bond energies stated to be devised for use in connection with what is called the "normal" covalence of the atoms. These are 4 for C, 3 for N and P, etc., in contradistinction, e.g., to pentavalency of P. Hence, for instance, the (mean) single bond energy of N−H is taken from the atomic heat of formation of NH_3, and in its ground level this molecule dissociates indeed into unexcited N and

[27] R. Samuel, "Report on absorption spectra and chemical linkage," Ind. Acad. Sci. (Bangalore, 1935). R. K. Asundi and R. Samuel, Proc. Phys. Soc. (London) **48**, 28 (1936). Asundi, Samuel, and Jan-Khan, Proc. Roy. Soc. **A157**, 28 (1936). R. Samuel *et al.*, Proc. Phys. Soc. (London) **48**, 626 (1936); **49**, 679, 568 (1937); E. Bergmann and R. Samuel, J. Org. Chem. **6**, 1 (1941).

[28] K. Butkow, Zeits. f. Physik **90**, 810 (1934).

[29] R. Samuel, Proc. Ind. Acad. Sci. **6**, 257 (1937).

3 unexcited H atoms. The bond energy therefore is identical with the adiabatic energy of dissociation. But this is not the case for CH_4 or SiH_4 as has been discussed above. The atomic heat of formation refers again to a system of unexcited atoms, but the ground level of CH_4 does not originate in the term of $C(s^2p^2)$ but of $C(sp^3)$, i.e., a highly excited term of the radical CH_2. What is called bond energy in such a case is not the energy necessary to remove H from C by an adiabatic excitation of the vibrational levels as before. It is a contribution to the heat of reaction counted from the (more or less arbitrary) level of the unexcited atoms.

From these remarks it is evident that we can safely compare the atomic energies of dissociation of bonds formed by C^2, N^3, S^2, and S^4, etc., among themselves, and probably also of those formed by C^4, Si^4, N^5, P^5, S^6, etc., among themselves. But as one group of values represents real energies of adiabatic dissociation, the other does not, it is by no means obvious whether a comparison from one group to the other is permissible.

Another point to be considered is the actual values of the single bond energies used. Only one of them may be mentioned here, i.e., that of the C−O bond. It is particularly interesting because on its value is based the calculation of the partial ionic character of many important molecules. As the C−O bond shows 22 percent ionic character, that of the C=O bond in the ketones, for example, is assumed to be about 44 percent. The ionic resonance energy of C−O is calculated as the difference of D(C−O) with the mean of the C−C and O−O bond and for the latter a value of 34.9 is calculated from $D(H_2O_2)$. However, this value is evidently unacceptable. The single bond energies of S−S and Se−Se are calculated to be 63.8 and 57.6, respectively, and there is only one sequence possible, that in which D(O−O) is higher than both. The dissociation energies of the double-bonded diatomic molecules* are directly known from the band spectra as $D(O_2)=117.4$, $D(S_2)=43.7$, i.e., in their proper order. As is well known from band spectra, hydrides behave differently from other molecules and exhibit an electron configuration closely approaching that of the "united atom." The too low value in H_2O_2 therefore probably is due to its bond energy bearing no relation to the linkages of oxygen to heavier atoms. As that of the S−S bond is independently calculated by Pauling from the S_8 molecule (that of Se−Se appears to be less certain), we may estimate D(O−O) as about three-quarters of $D(O_2)$ or about 72 kcal./mole. With such a value the ionic character of the C−O bond would be about 7 percent only.

A similar argument concerns the direct calculation of the resonance energy of the C=O double bond of the carbonyl group. The above value of $D(O_2)$ is that of the $^3\Sigma$ ground level, i.e., a structure with two unpaired electrons such as −O=O− or >O=O. We are not able to consider such a structure as partially due to a three-electron bond, but as a normal covalent bond disturbed and weakened by the unpaired electrons. This conception has been used to explain the strange increase of bond energy on excitation, known from the band spectra of many molecules. The excitation of an unpaired electron always increases the energy of formation of the molecule[30] whether such an electron is premoted (as in NO) or non-premoted (e.g., N_2^+), whether the nuclear fields are (nearly) equal and permit an explanation by means of a three-electron bond changing into another one, or whether the fields are unequal (e.g., AlO, AsO, SiF, SnCl, BeF, etc.) and no three-electron bond is possible. Hence, considering the $^3\Sigma$ term of O_2 not as a special case but as one of a great number of molecules with unpaired electrons, we shall estimate for the undisturbed structure $:\ddot{O}=\ddot{O}:$ ($^1\Sigma$) a value not lower but higher than $D(O_2)$, and according to the behavior of NO, a very considerable increase may be expected, again decreasing the ionic character of C=O to about 10 to 20 percent. Such a figure can be verified from the bond moment ($\mu=2.5$D) of the carbonyl group. To produce this moment, the group of 4 binding electrons has to be shifted 0.13A towards the O atom, or about 11 percent of the distance. To our

* In literature sometimes slightly different values are used for S_2. Cf. R. K. Asundi and R. Samuel, Proc. Ind. Acad. Sci. **3**, 466 (1936) and later references (27 and 29) for the above values.

[30] H. Lessheim and R. Samuel, Zeits. f. Physik **84**, 637 (1933); Phil. Mag. **21**, 41 (1936). R. K. Asundi and R. Samuel, Proc. Ind. Acad. Sci. **3**, 346, 467 (1936); **5**, 244 (1937).

mind, such bonds therefore are best described as covalent bonds with a slight polarity superimposed on them.

6. NATURE OF THE SPECTROSCOPICAL EVIDENCE

At the end of this necessarily lengthy analysis, the position which emerges from the maze of molecular constants, their working, and their separation into different additive components is quite clearly this: Neither the parachor (molecular volume), nor molecular refractivities, nor dipole moments, nor bond distances, nor bond energies are capable by themselves of distinguishing between different covalent chemical structures or the chemical theories (classical or wave mechanical) on which they are based. In all cases a grand total is observed empirically and in order to make any theoretical progress, it has to be divided into constituent increments for the individual atoms or bonds. This can be done in different ways and the resultant system of atom or bond constants is then automatically but arbitrarily adjusted to one out of two or more equivalent sets of chemical structures and equivalent chemical theories. It is possible unambiguously to differentiate between electrovalent and covalent linkage. But it is also quite evident that such molecular constants do not possess any diagnostic quality by which different types of covalent linkage could be discovered. This situation in fact has been predicted as an *a priori* probability some time ago[7b] and the reason given for it may now be assumed to have acquired some significance. Molecular constants like those mentioned are always due to the outside electrons of the molecule. Its "volume" is determined by its attractive and repulsive potential, its dipole moment by the dissymmetrical shift of the whole electron cloud, its internuclear distance is adjusted in such a way that the energy liberated on account of the interaction of the binding electrons becomes a maximum, etc. Such molecular constants therefore always measure some property of the molecule which is determined by and is a function of *all* its electrons or at least *all* its bonding electrons. But different types of the covalent linkage are distinguished by *an individual* electron playing a different role. Hence only such experiments *a priori* are capable of differentiating between them which permit us to observe the different parts taken up by an individual electron. Up till now such experiments are known only to spectroscopy where a particular spectrum is associated with the excitation of a single electron.

In this connection it is interesting to note that those additive molecular constants lead us further which permit us to utilize spectroscopical knowledge. The dissociation energy of a gaseous molecule like SO_2 or $SOCl_2$ into gaseous atoms may be determined thermochemically and then broken up into bond increments in various ways. But the dissociation spectra of these molecules which permit observation of the rupture of the individual bond directly select for us the correct among the possible systems of subdividing the total into additive bond energies. Again electric moments of organic molecules have been separated into bond moments only because one of them, the C−H moment, has been determined directly. Experimentally, this has been done, e.g., by Rollefson and Havens[31] from the variation of refractive index in the neighborhood of certain spectral lines, as suggested by Van Vleck.[32] Such a method utilizes rotational or vibrational but not electronic spectra. Consequently it may yield direct information on individual bond moments, yet it is incapable of giving a decision in such cases where the bond moment itself is well known, say of CO or −NC, but different interpretations are possible according to different theories involving the role of particular electrons.

Very similar conditions are met with in the attempt to utilize Raman spectra to distinguish between different structures. The Raman spectrum is useful to help to determine an unknown structure and will reveal whether, e.g., a particular double bond exists in the molecule. But again it is often unable to differentiate between two discordant interpretations of the same structure. A case in point is the Raman frequency of CO which is practically identical with that of N_2. Hence it was assumed to establish a triple bond between C and O, according to the formula C≡O. However, as was pointed out[33] this is entirely inconclusive as the Raman frequency is

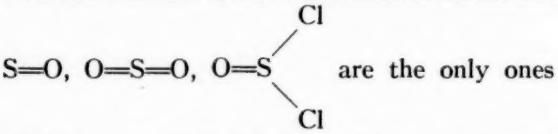
[31] R. Rollefson and R. Havens, Phys. Rev. **57**, 710 (1940).
[32] J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, New York, 1932).
[33] R. F. Hunter and R. Samuel, Chem. and Ind. **54**, 635 (1935).

that of an harmonic oscillator, which of course the molecule is not. In reality the force constant also depends on the anharmonic constant which can be measured only in the electronic spectrum. If this is taken into account, the bond energy (and together with it the true force constant of CO) turns out to be about 30 percent larger than that of N_2. Hence a triple bond for CO cannot be established this way, the only definite conclusion being that bond energies of oxides and nitrides are not commensurable.

From this follows that only electronic spectra are qualified to distinguish between different possible structures, as in principle they determine the electron configuration of the undisturbed molecule and give a description of the process of dissociation or formation.

On the other hand, on account of this intrinsic difficulty any inference as to different covalent structures of a particular molecule and its classical or wave mechanical interpretation by necessity must be inconclusive if based on measurements of such additive molecular constants. With very sincere respect for the great ingenuity exercised in the construction of such concepts, to our mind it is not acceptable to make these additive constants or some of them the sole arbiter either for the structure of a particular molecule or for a theory of valency.

Spectroscopical evidence is yet by no means complete, particularly as far as polyatomic molecules are concerned. Still, a definite body of facts already exists. For instance, the dissociation energy determined by spectroscopical means has the same value of about 116 kcal./mole for the S=O bond in the molecules SO, SO_2, $SOCl_2$, $SOBr_2$.[27] The valence vibration is about the same in SO and SO_2, both in the ground level and the first excited state, and the energy of excitation itself very nearly the same.[34] The same valence vibration even persists as Raman frequency of $SOCl_2$. Conditions are similar, e.g., for the S−Cl bond of the same molecules as also for other bonds in molecules formed by a central atom of another family. Even for radicals, i.e., molecules unknown to the chemist like SiCl and $SiCl_2$, the same close relation of bond energy, bond frequency, and energy of excitation appears to persist.[35] In our view it is therefore impossible to avoid the conclusion, that, for instance, the S=O bond is exactly of the same nature in SO, SO_2, and $SOCl_2$. This would exclude the three-electron bond for SO, formulae like $:\ddot{O}::\ddot{S}:\ddot{O}:$ or the resonance formula* {O=S—O, O—S=O}, and other similar ones. The classical structures



are the only ones which seem to meet the case. The experimental facts indicate electron-pair bonds, which are firmly localized between S and O. This also excludes any high ionic contribution, which is compatible only with fairly non-localized electrons. Indeed the bond moment of about 1.7D of SO_2 shows that the four binding electrons are shifted from the position of exact electrical symmetry towards O by 0.09A or about 6 percent of the bond distance.

All the other possible structures are suggested by particular values of additive molecular constants which are capable of different interpretations and therefore not conclusive. In such a case of conflicting results, to us it appears wiser to rely on the direct spectroscopical evidence and to accept the classical structures.

It is interesting to note that all such molecules for which similar conditions obtain, all for which we have direct spectroscopical evidence to this effect, and all of which are treated in this paper, are molecules formed by a definite and marked central atom (which mostly is capable of exercising different numerical valencies). Their behavior appears to be entirely different from that of the aromatic ring structures or others with conjugated double bonds, where only resonance formulae give a good approximation and where for this reason non-localized electrons exist. There appears to be some theoretical possibility of distinguishing between the wave functions of these two types;[7a] one great difference, however, is immediately evident. For the two resonating Kekulé formulae the energy difference is indeed

[34] Reference 27 and N. Metropolis, Phys. Rev. **60**, 295 (1941).

[35] R. K. Asundi, M. Karim, and R. Samuel, Proc. Phys. Soc. (London) **50**, 581 (1938).

* Cf. asterisk footnote on pages 187–188.

nil, but for the different structures formed by a central atom it is always several ev, and sometimes much more. Yet one or two ev are already of the order of some of the normal bond energies, like S−Cl, C−I, As−I, etc. It is therefore most probably not a good approximation to call structures with such a term difference energetically degenerated. It may well be that discordant interpretations of essentially the same concepts are caused by nothing more than that an energy difference of 1 ev seems small to the mathematical physicist, while 23 kcal./mole loom large in the mind of the spectroscopist or the physicochemist.

In accepting the classical structures, we also adopt its corollary, namely, that there exists only one kind of covalent linkage in this type of molecules. No proof of a coordinate or of any other second variety of covalent bond can be obtained from their chemical[3a] or physical behavior. The polarity which is always superimposed on the covalent bond by the dissymmetry of the nuclear fields is of the same order for all of them and constitutes a secondary effect at that. It does not justify the restoration of coordinate formulae by means of enhanced resonance.

This small polarity hardly appears to exceed 15 percent of ionic character at its very best. On this reduced basis the two concepts of a slight resonance with ionic structures or of a slight shift of the electrons towards the negative partner are of course equivalent. Which to employ is a question of usefulness. It may well be that the chemist concerned with the actions of the molecule prefers to depict it as resonating between two structures, each of which explains some of the reactions, while the physicist, observing one definite property of the undisturbed molecule such as its band spectrum, finds the other alternative more serviceable.

7. SUMMARY

(i). If additive molecular constants like molecular volume (parachor), molecular refractivity, dipole moments, bond distances, or bond energies are used to determine the structure of a molecule, the respective property of the molecule as a whole is measured and then separated into contributions of the constituent atoms or bonds. It is shown that this second step is arbitrary. All these constants retain their additive character even if entirely different structures of the molecule are assumed for the purpose of this separation.

(ii). In particular, all these constants are unable to distinguish between the set of classical structures recognizing only one type of covalent bond, and that of the theory of coordination in which some are described as semipolar double bonds, i.e., due to enhanced wave mechanical resonance with ionic parent structures. It is therefore not possible to differentiate between these two concepts or chemical theories by means of any of these constants.

(iii). This lack of diagnostic quality appears to have its origin in the fact that molecular volume or refractivity, electric moment, bond distance, and bond energy all are due to the action of *all* the electrons or at least *all* the binding electrons of the molecule. On the other hand, the difference between a normal covalent bond and a semipolar double bond, or the difference between resonating covalent or ionic structures, are due to the different part played by *a single*, individual electron, the action of which therefore cannot be observed or measured by such physico-chemical effects. The only experimental approach to such problems would then be through electronic band spectra which directly observe the different functional role of the single electron.

(iv). Among the structures which permit the perfect additive working of all these molecular constants are also those formed by pentacovalent nitrogen. As this hardly can be considered as a coincidence, the question as to whether pentacovalency of nitrogen is ruled out by wave mechanics is reinvestigated anew. It is shown that this is not so. The supposed covalency maximum of four of nitrogen is not established by any fundamental wave mechanical calculation, but is due to various assumptions or postulates introduced into the wave mechanical theory of valency in order to expand it from the calculable simple molecules to the more complex ones for which no calculation has been carried through. These assumptions may be replaced by similar ones which will permit the existence of pentacovalent nitrogen.

(v). The classical structures therefore appear to be entirely equivalent with any other set of

formulae. They are congruous with all observed facts and the results of actual wave mechanical calculation. They are favored by the results of spectroscopy which appear of particular importance. This paper is not concerned with aromatic or conjugated structures in which genuine resonance exists as the result of rigorous energetic degeneracy on account of non-localized electrons. But for (Werner's first-order) molecules marked by a distinct central atom—for which spectroscopy appears to indicate firm localization of the electrons—it is suggested that the classical formulae after all are the nearest approach to reality.

(vi). Consequently, for such molecules every bond is considered as a normal covalent bond. Its polarity now appears much reduced, e.g., to 13 percent ionic character in the nitro group or to 11 percent for the carbonyl radical. The polarity is therefore of the same order for all covalent bonds in such molecules and it is not possible to restore the concept of coordinate bonds for some of them on the basis of enhanced resonance with ionic structures.

Letters to the Editor

PROMPT publication of brief reports of important discoveries in physics may be secured by addressing them to this department. The closing date for this department is the third of the month. Because of the late closing date for the section no proof can be shown to authors. The Board of Editors does not hold itself responsible for the opinions expressed by the correspondents. Communications should not in general exceed 600 words in length.

The Effect of Non-Homogeneity of Molecular Weight on the Scattering of Light by High Polymer Solutions*

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March 14, 1944

THE treatment of light scattering in a previous letter[1] can be generalized to predict an observable effect which depends quantitatively on the non-homogeneity of the molecular weight and incidentally to demonstrate, as is known,[2] that the molecular weight so obtained is the weight average molecular weight.

We assume, in addition to the assumptions of the previous letter, that the refractive index is not a function of the size of the polymer molecule for a solution of given weight concentration, since index of refraction is a function of atomic groupings—not of the high polymer molecule. The turbidity is then the sum of the turbidities of each molecular weight species which will be denoted by the running index i. Equation (2) of the previous letter then becomes

$$\tau_2=\sum_i \tau_{2,i}=\frac{32\pi^3 M_1 n^2\left(\frac{\partial n}{\partial g}\right)^2}{3N_0\lambda^4\rho}\sum_i \frac{g_i}{\left(-\frac{\partial \ln f_1}{\partial g_i}\right)}, \tag{1}$$

where g_i is the weight concentration of i in the species and $g=\Sigma_{gi}$ is the total concentration.

We represent the osmotic pressure by the following equation:

$$\pi=\sum_i \frac{RT}{M_i}g_i+Bg^2+Cg^3+\cdots. \tag{2}$$

Numerous measurements[3,4] have shown B to be independent of molecular weight for a given system and C is assumed to be constant in the molecular weight range used. It follows, then, that

$$-\frac{\partial \ln f_1}{\partial g_i}=\frac{M_1}{\rho RT}\frac{\partial \pi}{\partial g_i}=\frac{M_1}{\rho}\left(\frac{1}{M_i}+\frac{2B}{RT}g+\frac{3C}{RT}g^2\right) \tag{3}$$

and

$$\tau_2=\frac{32\pi^3 n^2\left(\frac{\partial n}{\partial g}\right)^2}{3N_0\lambda^4}\sum_i \frac{g_i}{\frac{1}{M_i}+\frac{2B}{RT}g+\frac{3C}{RT}g^2}. \tag{4}$$

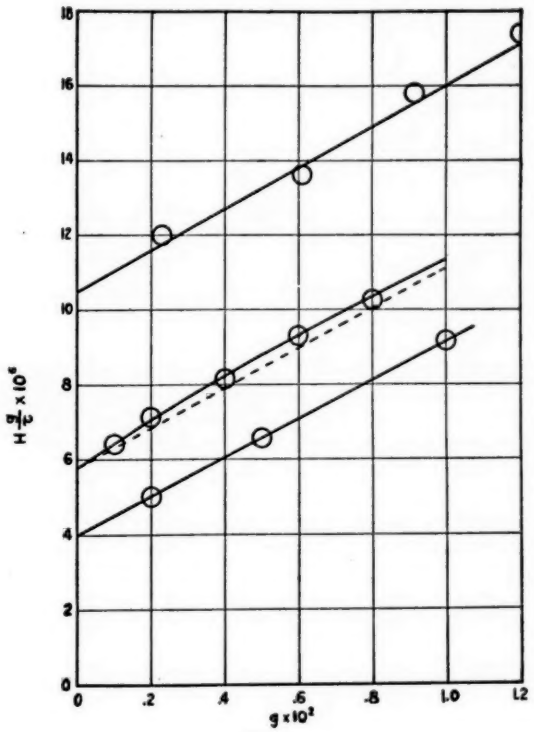

FIG. 1.

Let γ_i equal the weight fraction g_i/g of the ith species and $\Sigma\gamma_i=1$. Using this and rearranging, (4) becomes with the abbreviation $1/H$ for the constant coefficient,

$$\frac{g}{\tau_2}=\frac{1}{H}\left\{\frac{1}{\sum_i \frac{M_i\gamma_i}{1+\frac{2B}{RT}M_i g+\frac{3C}{RT}M_i g^2}}\right\}. \tag{5}$$

Expanding this in a MacLaurin series in g we obtain

$$H\left(\frac{g}{\tau_2}\right)=\frac{1}{\sum_i M_i\gamma_i}+\left[\frac{2B\sum_i M_i^2\gamma_i}{RT(\sum_i M_i\gamma_i)^2}\right]g + \left[\frac{4B^2(\sum_i M_i^2\gamma_i)^2}{R^2T^2(\sum_i M_i\gamma_i)^3}-\frac{\sum_i\left(\frac{4B^2M_i}{R^2T^2}-\frac{3C}{RT}\right)M_i^2\gamma_i}{(\sum_i M_i\gamma_i)^2}\right]g^2. \tag{6}$$

The denominator of the first term of the expansion is the weight average molecular weight $\bar{M}$.

If we set $M_i=\bar{M}+\Delta M_i$ and note that

$$\sum_i \Delta M_i\gamma_i=0,$$

Eq. (6) can be written in the following form:

$$H\left(\frac{g}{\tau_2}\right)=\frac{1}{\bar{M}}+\frac{2B}{RT}\left[1+\left\langle\left(\frac{\Delta M}{\bar{M}}\right)^2\right\rangle_{Av}\right]g + \left\{\frac{3C}{RT}\left[1+\left\langle\left(\frac{\Delta M}{\bar{M}}\right)^2\right\rangle_{Av}\right]+\frac{4B^2\bar{M}}{R^2T^2}\left[\left\{\left\langle\left(\frac{\Delta M}{\bar{M}}\right)^2\right\rangle_{Av}\right\}^2 - \left\langle\left(\frac{\Delta M}{\bar{M}}\right)^2\right\rangle_{Av}-\left\langle\left(\frac{\Delta M}{\bar{M}}\right)^3\right\rangle_{Av}\right\}g^2+\cdots \tag{7}$$

where

$$\left\langle\left(\frac{\Delta M}{\bar{M}}\right)^2\right\rangle_{Av}=\frac{\Sigma\,\Delta M_i{}^2\gamma_i}{\bar{M}_2}\text{ etc.}$$

This equation indicates that the dispersion of the molecular weight influences the slope and curvature of the plot of $H(g/\tau)$ *versus* g.

We have mixed in equal weights two of the fractions mentioned in the previous letter and carefully measured the turbidity of the mixture in methyl ethyl ketone. The intercept of the mixture corresponds to a molecular weight of 172,500 which is equal to the weight average ½ (95,000 +250,000) = 172,500, the excellent agreement being fortuitous.

The curved line in Fig. 1 is a plot of Eq. (7), the constants having been evaluated from the slopes and intercepts of the pure fraction lines, assuming C is zero. For comparison, the lower (straight) line represents the plot which would be expected if the width of the mixture were not taken into account; that is, its slope is the average of the two pure fraction lines. Our data follow well the plot of Eq. (7), but our precision is not sufficient to consider this as more than an indication of the correctness of Eq. (7).

We have confirmed experimentally that the measurement of turbidity yields the weight average molecular weight and the above treatment indicates that with the aid of more precise apparatus (now under construction) a measure of the width of the distribution curve may be obtained.

The work of Debye referred to in the previous letter[1] appears in the April issue of the *Journal of Applied Physics*.

* Publication assisted by the Ernest Kempton Adams Fund for Physical Research of Columbia University.

[1] P. M. Doty, B. H. Zimm, and H. Mark, J. Chem. Phys. **12**, 144 (1944).

[2] P. Debye, private communication.

[3] T. Alfrey, A. Bartovics, and H. Mark, J. Am. Chem. Soc. **65**, 2319 (1943).

[4] H. Mark, *Physical Chemistry of High Polymeric Systems* (Interscience Publishers, Inc., New York, 1940).

Erratum: An Application of Probability Considerations to the Mechanism of the Photochemical Polymerization of Acetylene

[J. Chem. Phys. **12**, 37 (1944)]

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